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# THE DEVELOPMENT OF PRACTICAL SYSTEMS FOR $^{14}C$ MEASUREMENT IN SMALL SAMPLES USING MINIATURE COUNTERS

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ABSTRACT. Miniature gas counters have been in use since the early 1960s for the measurement of $^{14}C$ but were for a long time seen as suitable for providing approximate indications of activity rather than measurements for more precise dates. In recent years the need for better measurements of small samples has posed a continuing challenge for the $^{14}C$ laboratories. This paper examines how the challenge has been met across the world using conventional beta decay counting techniques and proportional gas counters of 50ml volume or less. A survey is made of the rise of these techniques and attention paid to the solution through modern technology of earlier problems. Some practical systems, now in routine use, are described and consideration is given to the future for miniature counter measurements. Such systems have several attractive features that will guarantee their usefulness in $^{14}C$ measurements for the future.

## INTRODUCTION

The continuing interest in the measurement of small samples is reflected in the number of papers presented at this conference. To a large extent this must be due to the increased number of laboratories which are now successful with the accelerator mass spectrometer method. It is not our intention to detract, in the slightest, from the exciting progress of this method. It is appropriate at this time to report on the developments of the alternative systems which, using miniature gas proportional counters, have also made exciting steps forward in small sample measurements, achieving now on a routine basis a precision and turnover which, even less than ten years ago, was hardly contemplated.

We outline here the developments and highlight the features of the modern technology that make light work of what, earlier, were almost insurmountable challenges. We also describe the essential features of some contemporary systems, principally that of Harwell, and summarize the current world position on the use of small counters. Finally, we comment on the likely future for this technique.

## BASIC IDEAS

First, the basic requirements of practical systems designed for small sample measurements using conventional beta-decay counting methods, should be put into perspective. Most are the usual requirements of any low-level nuclear counting applications. The difference is only in the scale of two principal factors, 1) much smaller quantity of material available in the chemical preparation procedures and, 2) much longer counting when everything must remain stable to obtain a worthwhile result. Table 1 illustrates the requirements of quantities of carbon according to counter sizes.

The definition of a miniature counter is obviously arbitrary. Generally, ca 50ml volume is taken as the limit. At Harwell 5ml volume counters are 'micros' and the 30ml counters are 'minis'. Thus, the range goes from 2.7mg carbon required to fill a 5ml 'micro' to 1 atmosphere with $CO_2$ or $CH_4$, to ca 80mg to fill a 30ml 'mini' to 5 atmospheres (Table 1). Following from this, taking the disintegration rate of "modern" carbon as 13.56dpm/g (Karlen *et al*, 1966), the comparable counting time in days to obtain the precisions, in this case, just Poisson counting statistics on the sample count, is shown in Table 2. These are clearly minimum times, as there is more to an error estimate than simply the counting statistics. Also archaeologic or geologic samples will produce proportionally lower counting rates than the "modern" samples given.

The numbers illustrate, however, that the key to success is the design of a system that fulfills the following objectives: 1) the very lowest and stable background, 2) the highest counting efficiencies to give the maximum signal to background ratios, 3) long-term stability in all the system parameters, 4) multiplication of counter detectors to obtain a worthwhile annual turnover of samples measured.

There is nothing new in any of these requirements except perhaps that previously multiplication of the counters, although desirable, was not possible. Counters required a rack of instruments 1m high, not just a chip or two as today. We would like to stress here the importance of persevering with improvements to detail in well-established techniques, combined with modern technology in revolutionizing practical systems for the measurement of milligram-size samples.

## HISTORICAL BACKGROUND

1976 is a key date as it was just around this time that the talk of measurement of small samples by mass spectrometry produced a revival of interest in conventional gas counter methods. 1982 is another focal point because it saw the fruition of considerable evidence for feasibility of experimental small counter systems and, finally, the last three years have been witness to the development and maintenance of routine operation of these systems.

Table 3 summarizes developments before 1976. The earliest papers (Oeschger, 1963; Kohman & Goel, 1963) describe very different counter designs. Oeschger used a small thin-walled counter similar to his famous screen-wall counters with the anticoincidence and sample gas volumes in a

TABLE 1
Quantity of carbon as $CO_2$ or $CH_4$ required (milligrams)

| Size of counter (ml) | 1 atm | 2 atm | 3 atm | 4 atm | 5 atm |
|---|---|---|---|---|---|
| 5 "micro" | 2.7 | 5.4 | 8.0 | 10.7 | 13.4 |
| 10 | 5.4 | 10.7 | 16.1 | 21.4 | 26.8 |
| 15 | 8.0 | 16.1 | 24.1 | 32.1 | 40.2 |
| 30 "mini" | 16.1 | 32.1 | 48 | 64.3 | 80.3 |

TABLE 2

Time (days) to achieve various Poisson counting precisions (assuming 90% counting efficiencies)

| Quantity of carbon (mg) | 10% | 3% | 1% |
|---|---|---|---|
| 5.4 | 1 | 12 | 105 |
| 10.7 | 0.5 | 6 | 53 |
| 24.0 | | 2.5 | 24 |
| 32.0 | | 2 | 18 |
| 64.3 | | 1 | 9 |

single envelope. Kohman used a quartz envelope counter designed earlier by Stoenner, Schaeffer and Davis (1960) which was the forerunner of the present Brookhaven counters used in the Harwell system. Geyh (1967) described a different integral design using a plastic phosphor for anticoincidence with the sample counter formed from a re-entrant cavity, lined with aluminium foil, bored into it. Memory effect and gas poisoning due to outgassing seems to have been the main limitation of this design.

Of the early applications of small counters it is noted that Kohman measured terrestrial ages of cosmogenically produced meteorites and Oeschger dated occluded $CO_2$ in glacial ice (Oeschger *et al*, 1966) with their miniature counters. Only 1 to 2 tons rather than 10 to 20 tons of ice was needed with the new counter! Oeschger (1963) reflected the general attitude toward miniature counters at this time, "radiocarbon dating becomes possible if not too high an accuracy is required." In line with this, Currie, Noakes and Breiter's work (1978) only required relatively low precision, ca 15%, in measuring $^{14}C$ in atmospheric aerosols.

The underlying reason for lack of precision seems to have been the

TABLE 3

Characteristics of some early miniature gas proportional counters used for $^{14}C$ measurements (up to 1976)

| Counter type | Volume ($cm^3$/gas) | Pressure (atm) | Back-ground (cpm) | Modern carbon to background ratio* | Reference |
|---|---|---|---|---|---|
| Integral gas anti-coincidence (thin wall) | 40/$CO_2$ | 0.92 | 0.15 | 1.3 | Oeschger (1963) |
| Quartz tube (Brookhaven) | 42/$CO_2$ | 1.0 | 0.28 | 0.6 | Kohman & Goel (1963) |
| Integral plastic scintillator anti-coincidence | 40/$C_2H_6$ | 1.0 | 0.25 | 1.2 | Geyh (1967) |
| Integral plastic scintillator anti-coincidence | 52/$CH_4$ | 1.0 | 0.29 | 1.3 | Tykva (1967) |
| Quartz tube | 15/$CO_2$ | 1.2 | 0.17 | 0.4 | Currie (ms) Currie, Noakes & Breiter (1978) |

*Normalized to 'modern' as 13.56 dpm/g (Karlen *et al*, 1966) unfavorable signal:background ratios; signal, meaning the count rate obtained for an equivalent modern sample (the ratio refers to modern: background therefore here). Table 3 shows very reasonable values of background (B) for counters of the volumes (V) compared to the ultimate estimated theoretical background values ($B = 0.013\ V^{2/3}$) (Oeschger & Loosli, 1975) but modern:background ratios of only around unity. The principal factor here appears to be the filling pressure.

No archaeologic applications for miniature gas counter measurements were reported in the early years. Impetus to try seems to stem from the earliest discussion of the possibility of measuring small samples by accelerator mass spectrometry! Leaders in this field were Harbottle, Sayre and Stoenner (1979) who resumed work on an archaeologic project they had considered some years before with support from the Smithsonian Institution. Low-level measurements of beta-emitting isotopes other than $^{14}C$ had been a speciality of their laboratory (Brookhaven) and included $^{39}Ar$ measurements associated with the search for the elusive solar neutrino and measurement of cosmogenically produced isotopes in samples returned from the lunar missions.

The precision required for archaeologic dating was obviously much higher than anything attempted in the earlier work, since to get a result to better than ±80 years a precision of better than ±1% is required. There was much to be done to get beyond the earlier applications of miniature counters, in which only approximate results were expected.

Harbottle and co-workers designed a counter which, in addition to having as low a background as possible, would maintain stable counting over a long enough period to achieve good counting statistics. Using $CO_2$ as counting gas perhaps made this task harder; $CO_2$ was notoriously difficult to keep free from electronegative impurities that build up during the counting period from the outgassing of materials of which the counter may be constructed and, eventually, poison the gas; plastics and greases are particularly bad in this respect. However, the chemistry involved in preparing $CO_2$ from organic and carbonate samples was attractively simple, its purification well researched and successful in large gas counters for the highest precision measurements attainable (eg, ±1‰). It is also an ideal gas for transporting around gas handling systems cryogenically.

Their counter was made of high purity materials: suprasil quartz tube, pure copper (later iron) foil cathodes; they used a filling procedure which compressed the gas into the sensitive volume of the counter with a mercury piston, the mercury eventually passing through the stopcock and stopping just short of the sensitive volume at a constriction in the tube. In this way the counting gas was completely isolated from the stopcock grease and the dead volume reduced to an absolute minimum. To this end the voids in the termination legs were also filled with mercury. Thus, the losses in the complete process from chemical preparation through filling the counter are negligible with virtually all carbon extracted from the sample transferred to the counting volume.

Between every filling the counter volume could be outgassed under vacuum while heated to 400°C with a small tube furnace above the mercury levels in the termination legs. Possible build-up of impurities from repeated filling and memory effects were thus obviated. The result was a counter which, in addition to having a low background, showed no deterioration in gas counting quality after months and even years of counting.

The next problem was to increase the modern:background ratio which was achieved 1) by increasing the filling pressure to 4 atmospheres, thereby improving the modern:background ratio to over 3; this required a much finer anode wire (0.79$\mu$m diameter) than previously used to keep the operating EHT voltage to within reasonable levels, and 2) by considering new ways of obtaining an even lower background. A significant reduction occurred when a large NaI crystal (240mm long by 240mm diameter) was used for the anticoincidence guard shield. A dramatic reduction from 0.039 to 0.015cpm was obtained giving a corresponding multiplication of the modern:background ratio from 3.3 to 8.9.

It was clear that several such counters would have to run simultaneously to measure at least 100 samples per year. Such a system for high precision measurements with large counters was already operating successfully in Heidelberg since 1979 (Schoch *et al*, 1980). At Harwell we made the decision to set up such a multi-counter system dedicated to small sample measurements. In view of the very large gap between the fail point of the liquid scintillation system (1g) and the capability of the Brookhaven microcounter (10mg), it seemed appropriate to consider the use of an intermediate size or sizes for faster counting turnaround times. On Brookhaven's advice, a second size counter (30ml, 64mg carbon with 4 atmospheres $CO_2$ filling) was agreed upon. Brookhaven, too, agreed to construct and supply the counters for our planned system. Six of each of these were arranged in a single anticoincidence guard counter, a 305mm NaI crystal 305mm long by 305mm diameter (Fig 1). Each counter is housed in its individual copper box which facilitates removal for counter filling changes and eliminates cross-talk interference between neighboring counters. This assembly comprised the first production facility for small sample measurements and was brought into routine operation in November 1981.

Table 4 summarizes developments from 1976 to 1982. The main differences are higher pressures which were generally adopted and lower backgrounds, *pro-rata* for the counter sizes in some cases, with both factors reflected in the generally higher modern:background ratios. Innovations in techniques had also begun such as the use of the large NaI crystal as the active guard counter.

In planning the routine facility at Harwell, the NaI crystal has seemed an obvious necessity if as good modern:background ratios as Brookhaven were to be achieved, especially since the laboratory is a one-story building. It is now clear that this decision was vital to the success of the system. The reasons for a lower background in the crystal were not clear and are still probably not fully understood. To date we have examined the spectra and, in particular, the parts which are useful in registering coincident pulses with the gas counters being shielded. The results are given in Figure 2. Figure 2A shows the distribution of the pulses which are not in coincidence with those from the sample counter but which represent the total spectrum

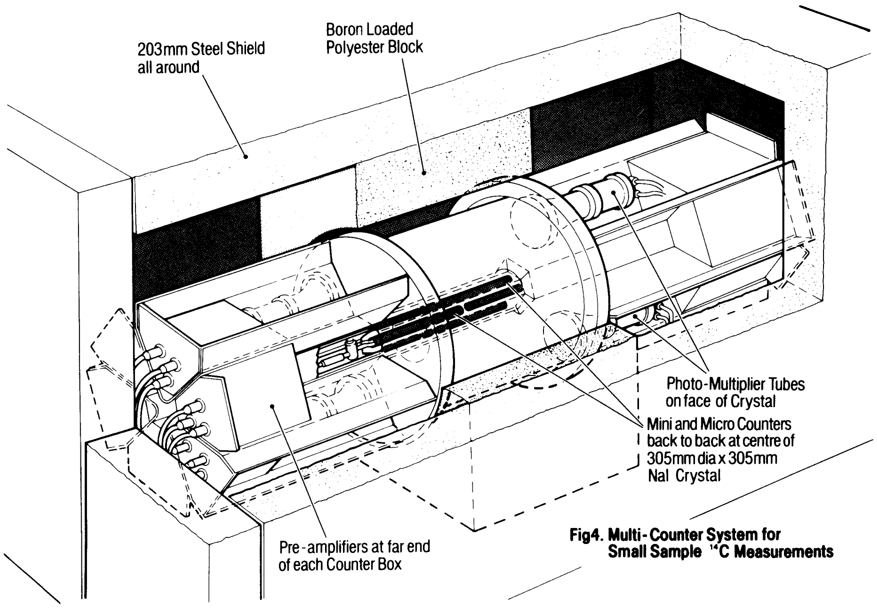


Fig 1. Multi-counter system for small sample $^{14}C$ measurements

of the crystal. Of the total count rate, ca 5000cpm, 80% of counts, lie in the lower region up to 3MeV ($\gamma$ rays and bremmstrahlung), 9% in the region 3MeV to 35MeV and 11% in the region >35MeV, which form the well-defined peak at ca 35MeV. This peak is due to the energy deposited by the passage of the cosmic muons through the large crystal.

Figure 2B shows the fraction of the pulses which are in coincidence with those from the sample counter and thus, useful in producing background reductions. As expected, most coincidences are produced by the muon pulses and, in this respect, the crystal is no more efficient than any gas proportional or plastic phosphor shield counter. The difference lies in the lower $\gamma$ ray energy region where another group of pulses occurs in the coincident spectra of the crystal. Without these, the background of a typical microcounter changes from ca 0.02cpm to ca 0.08cpm. It is assumed that these pulses are due to Compton scattered $\gamma$ rays originating from $\gamma$ ray interactions in the sample counter itself, primarily in the quartz envelope and metal cathode. Thus, the interaction produces an electron in the counter volume but the pulse it makes is cancelled by detection of the scattered $\gamma$ ray in the crystal.

It could be argued that the impurities in the crystal introduce these gammas (see the $^{40}K$ peak) but this cannot be the whole story or the lower backgrounds would not be obtained. That they are lower has also been verified from comparative tests with other counters, a reduction of from 0.2cpm to 0.06cpm was reported compared to our crystal and a plastic phosphor assembly with the Wallac copper counter (Kaihola *et al,* 1983). Loosli, Forster and Otlet (1986) describe an experiment with the second

TABLE 4
Characteristics of new systems reported post 1976 to 1982

| Counter type* | Volume (ml) | Filling pressure (atm – gas) | Background (cpm) | Modern to background ratio | Shield | Group/date (ref) |
|---|---|---|---|---|---|---|
| Q | 5 | 4 – $CO_2$ | 0.039 | 3.3 | Conventional | Brookhaven, USA/1977 |
| Q | 5 | 4 – $CO_2$ | 0.015 | 8.9 | NaI | (Harbottle, Sayre & Stoenner, 1979) |
| C | 15 | 3 – $CH_4$ | 0.170 | 1.5 | Conventional | Univ Washington, USA/1981 (Sheppard, Hopper & Welter, 1983) |
| Q | 5 | 4 – $CO_2$ | 0.021 | 6.2 | NaI | Harwell UK/1981 |
| Q | 30 | 4 – $CO_2$ | 0.087 | 8.0 | NaI | (Otlet & Evans, 1983) |
| C | 10 | 4 – $CH_4$ | 0.20 | 1.3 | Plastic phosphor | Univ Turku, Finland/1982 |
| C | 10 | 4 – $CH_4$ | 0.06 | 4.3 | NaI (Harwell) | (Kaihola *et al*, 1983) |
| C | 5 | 4 – $CO_2$ | 0.058 | 1.8 | Conventional | NBS, USA/1982 |
| C | 18 | 2 – $CO_2$ | 0.152 | 0.7 | Conventional | (Currie *et al*, 1983) |
| C | 5 | 4.5 – $CO_2$ | 0.084 | 1.6 | Conventional | R B Inst, Yugoslavia/1982 (Srdoc, Obelic & Horvatincic, 1983) |
| Q | 35 | 1 – $CO_2$ | 0.273 | 0.8 | Conventional | Univ Groningen, Netherlands/1982 |
| C | 35 | 1 – $CO_2$ | 0.380 | 0.5 | Conventional | (Hut, Keyser & Wijma, 1983) |

*Key: Q Quartz tube
C Copper tube

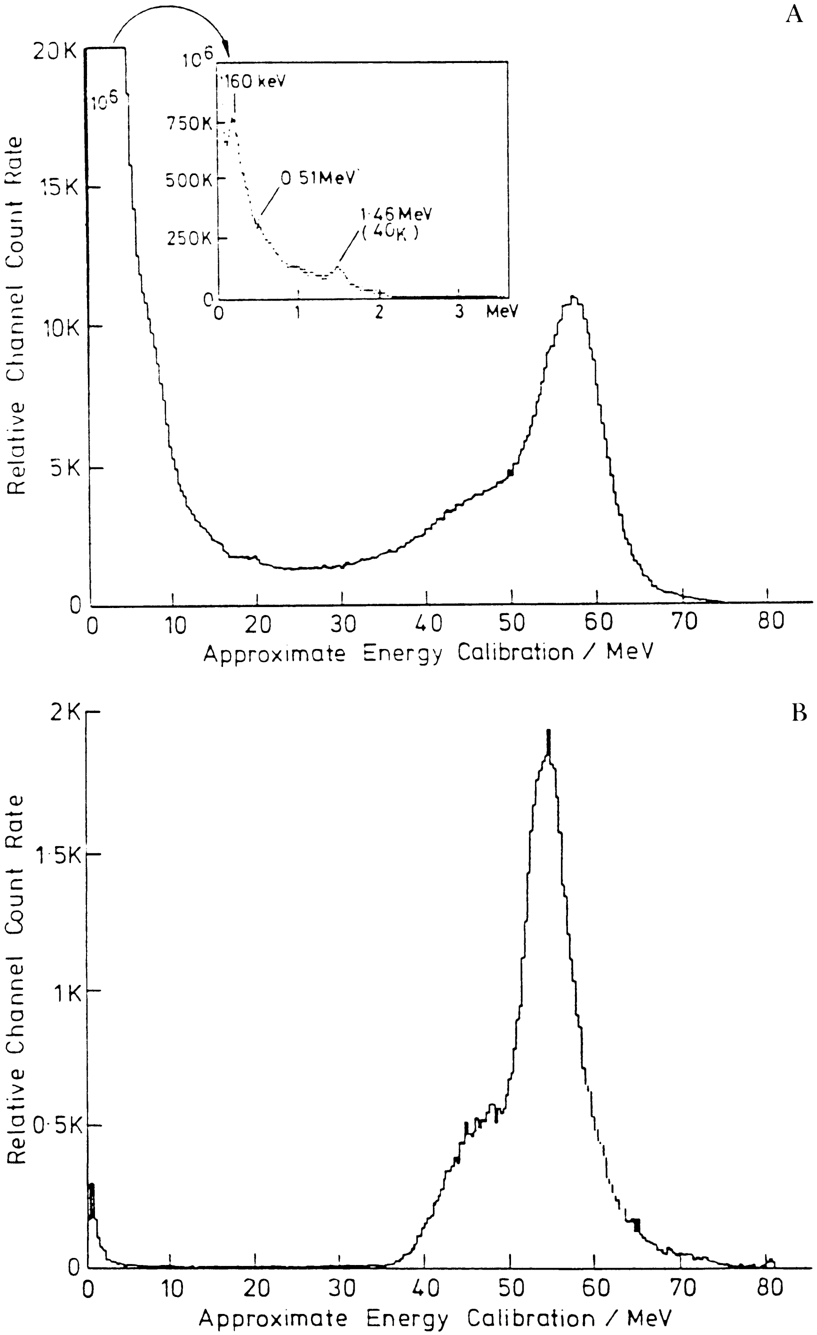


Fig 2. Guard counter (NaI) spectra.
A. Events not in coincidence with sample (gas) counters.
B. Events in coincidence with sample (gas) counters.

Harwell crystal compared with a shield of the Bern underground laboratory and a plastic phosphor guard counter assembly in Munich, using a Brookhaven counter and two Bern $^{39}$Ar counters.

Another recent innovation is in the procedures used for data acquisition and quality control analysis where the introduction of the on-line micro/mini computers clearly make their impact. Currie *et al* (1983) use event by event recording of the data pulses. Some analysis can be carried out on-line during the counting session, eg, pulse rise time analysis, and the data can be replayed from the disk and analyses of correlations with additional interconnecting parameters carried out. One very useful feature of this method is the ability to carry out pulse interval time analysis, a powerful procedure for checking if Poisson statistics are being obeyed.

Another method used at Harwell is recording the full pulse height spectrum of the number of coincident (muon) and anticoincident (electron) pulses in two, 256-channel locations, 0 to 255 covering the energy range ca 0.3 to 60keV with everything above that being dumped in channel 256. Such a display is useful for the initial gain setting of a new gas filling (using an $^{241}$Am source to excite a K $\alpha$ spectrum, 6.4keV, off the iron cathode) and also provides valuable information on gas quality and gain stability throughout the counting time (Otlet *et al,* 1983; Otlet, Sanderson, & Walker, in press). Periodic dumping to disk ensures no total loss of data through mishaps.

A survey taken in May 1985 is shown in Table 5. All laboratories report continued use of their counter systems since 1982 and most have incorporated detail improvements which give improved performances. Two new laboratories have installed major small counter systems (see Jelen & Geyh, 1986).

There are at least 9 institutions representing 8 countries using small counter systems and at least one in the Soviet Union (Alexeev & Ivliev, 1981). Apologies are offered to those not included in Table 5 where the details of only the latest installations are listed.

The system from the University of Turku, now delivered to The Australian National University offers yet another cosmic guard counter design

TABLE 5
Latest 'stop press' developments

| Group | No. of counters | Sample size (mg) | Modern to background ratio | Guard system and data acquisition |
|---|---|---|---|---|
| Univ Turku, Finland (ANU, Australia) | 14 | 27 | 4 | Liquid scintillation event by event (rise time analysis) |
| NLB, Hannover FRG | 10 | 22 | 10 | 2, NaI (152 mm × 152 mm) five channels recording (channels ratio analysis) |
| Harwell, UK | 12 (+ 12) | 10 | 10* | 2, NaI (305 mm × 305 mm) |
| | | 66 | 15* | Coincidence/anticoincidence microcomputer based MCA (spectral analysis) |

*Improved results obtained from second crystal and new Brookhaven counters possibility (Kaihola *et al*, 1984) this time using a liquid scintillation detector. The NaI crystal still remains in favor at Harwell and the results reported for smaller crystals in Hannover are very impressive. The latest results for a crystal that will be put into use in the second Harwell system, bringing our total of counters to 24 are also presented. It is pleasing to quote the highest ever modern:background ratios for this system and the improvements which the Harshaw Chemical Company were able to get in reducing the intrinsic activity of this crystal by a factor of ca 3 should be acknowledged and also the help of colleagues in Brookhaven whose latest set of quartz tube counters give even lower backgrounds.

## SUMMARY AND CONCLUSIONS

We have presented a progress report on the use world-wide of miniature gas proportional counters for $^{14}C$ measurements. Originally regarded as suitable only for approximate measurements, the counters are now routinely used for archaeologic and other relatively high-precision measurements. Success is attributed to several factors which include:

1) New counter designs which have lower intrinsic backgrounds and operate at higher pressures for long periods;

2) New concepts in active shield designs (eg, NaI) which give even lower background and hence higher modern:background ratios;

3) Electronic systems using chip technology which facilitate multi-counter operation;

4) Data acquisition systems and data analysis by micro/mini-computers which give confidence and higher precision through on-line quality control. How miniature counters systems would fare once the accelerator mass spectrometers really got under way was a question often asked in the past. We can now say they continue to fulfill an important role probably mostly because their installation and operating costs are inevitably a fraction of that of their AMS counterparts. Further, many institutions prefer making measurements in their own laboratories. It should also be noted that the labor involved in processing samples for the small counters is considerably less than for the conventional large sample counter systems (especially liquid scintillation counting) and therefore represents an additional attractive feature. Thus, with modern:background ratios as good as the average liquid scintillation system, an increasing use of small counters for general purpose, routine, archaeologic/geologic measurements is also foreseen.

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