

# ON A NEW METHOD FOR INTRODUCING NATURAL C<sup>14</sup> IN A LIQUID SCINTILLATOR

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## INTRODUCTION

LIQUID scintillation counting provides one of the most accurate methods of radiocarbon dating. In this method a suitable compound prepared from the sample to be dated is introduced in a liquid scintillator. A high detection efficiency for the C<sup>14</sup> beta-radiation is thus realized. The carbon may be

TABLE I

Methods				Results		
				Contemporary rate counts/min	Back-ground counts/min	Maximum age (years)
Hayes	Coincidence— anticoincidence	90 ml	Cymene from terpenes	470	60	48,000
Arnold	Cooling Coincidence circuit	100 ml	hexane octane	182	26	44,000
Audric	Cooling Coincidence circuit	80 ml	acetylene	45	40	31,000
Pringle	Selection of photo- multiplier tubes— selection of pulses	20 ml	toluene C <sup>14</sup> H <sub>8</sub>	15.5	3.3	33,000
			methanol	14.2	6.2	29,000
			methyl- borate	10.07	4.26	30,000

<sup>1</sup> Counting period: 24 hr. for the sample and for the background.  
 Limit: 4  $\sigma$  ( $\sigma$ : standard deviation in the background counting rate).

introduced either as the solvent component of the liquid scintillator or as a diluent. In the latter case one must introduce sufficient quantities without severely quenching the scintillator. Furthermore, in any case, in order to

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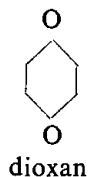
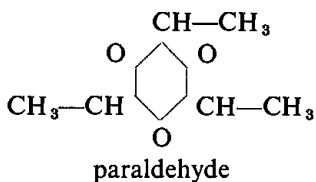
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introduce the maximum quantity of the carbon of the original sample it is best to choose a compound in which all the carbon atoms originate from the sample. Several workers have already worked along this line and the technique used differ from each other, by the choice of the synthesized component, the liquid scintillator and the electronic device associated with the photomultiplier. In Table 1 are given some of the results published up to now and an abstract of the techniques involved.<sup>1-8</sup>

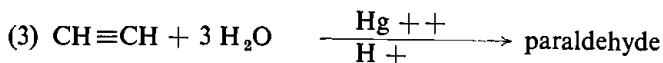
#### DESCRIPTION OF PROPOSED METHOD

In a search for a new compound to be introduced in a liquid scintillator we first considered benzene which is a fairly good solvent from the point of view of scintillation.<sup>9</sup> The six carbon atoms of benzene could be derived from acetylene by trimerization in presence of Reppe's catalyst:<sup>10</sup>  $(C_6H_6)_3$  PNi  $(CO)_2$ . However, although the method was successfully applied to the synthesis of radioactive benzene on a 10 mmole scale<sup>11</sup> we did not investigate further this process on account of foreseen difficulties in the manipulation of large quantities of acetylene under 15 atm pressure. However, at the time of writing this paper, has appeared a note<sup>12</sup> on the trimerization of acetylene at room temperature and sub-atmospheric pressure and we intend to use this method for radiocarbon dating.

We then turned to paraldehyde, the trimer of acetaldehyde, since, owing to its cyclic structure it is closely related to that of dioxan which has already been used as a diluent in various liquid scintillators.<sup>9</sup>



This choice was also made on the basis of the following considerations:  
 — paraldehyde may be prepared in a single-step from acetylene according to VOGT and NIEWLAND.<sup>13</sup>



so that the six carbon atoms are derived from barium carbonate.

— paraldehyde is fairly stable when neutral and does not hydrolyze like methyl borate.<sup>5</sup>

— paraldehyde has a high percentage of carbon (54%) so that it was expected to introduce a high amount of original carbon into a small volume of scintillator.

## PARALDEHYDE AS A DILUENT IN A LIQUID SCINTILLATOR

We first examined the influence of various amounts of paraldehyde in two liquid scintillators the 'fluors' of which are PPO; 4 g/l. + POPOP; 0.1 g/l. (a) in xylene as primary solvent (b) in xylene to which naphthalene (300 g/l.) was added as a secondary solute. The variations of efficiency are given in Fig. 1. As reported by KALLMANN<sup>7</sup> the addition of naphthalene increases notably the efficiency. These curves were obtained with a  $50 \mu\text{C Cs}^{137}$  source.

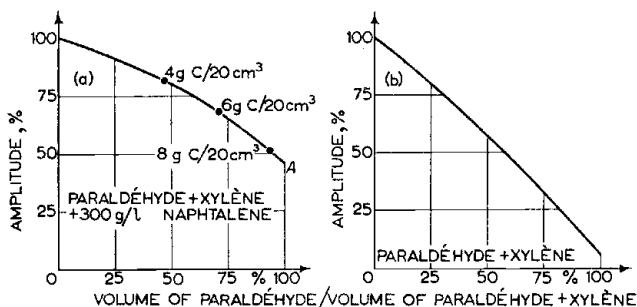


Fig. 1. Pulse height vs. paraldehyde concentration:  
I with 300 g/l. naphthalene.  
II with naphthalene.

From these preliminary experiments the following solvent was used later: paraldehyde 72.3%, xylene 4.4%, naphthalene 23.3%. This corresponds to 8 g of carbon for a 20 ml scintillator without added paraldehyde.<sup>14</sup>

The scintillator was placed in a quartz cell as we observed in a Pyrex glass cell a 'background' of 30 impulses/min corresponding to energies higher than 50 keV and 6 impulses/min in the energy band 50–150 keV due to appreciable amounts of  $K^{40}$  in Pyrex. The quartz cell was silvered outside, the layer of silver being protected by a white paint. In order to reduce the quenching due to dissolved oxygen, pure nitrogen was bubbled through the scintillator. Use of an optical joint (silicone oil Dow Corning S.I. 200, 30,000 cS) between the cell and scintillator, was made.

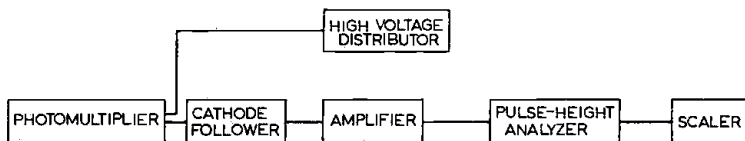


Fig. 2. Block-diagram of counting apparatus.

A block-diagram of the electronic device used is given in Fig. 2. The selected photomultiplier E.M.I. 6097 has the highest possible signal to noise ratio. The voltage across the dynodes was set in accordance with this requirement. The pulses pass to a 2 MHz amplifier with a maximum gain of 20,000

through a 'cathode follower' and then to a pulse height analyzer the resolution time of which is  $1 \mu\text{sec}$ . The width band of the analyzer is chosen for the selection of only those pulses in the range of energies corresponding to  $\text{C}^{14}$  beta spectrum. The value of the superior threshold allows the elimination of pulses corresponding to an energy superior to 150 keV; the choice of the inferior threshold being made in accordance with the background of the photomultiplier and the stability of the electronic device. This is why the selection of the phototube is so important to obtain valuable results. The energy calibration of the scintillator was made with the pulses of a  $\text{Cs}^{137}$  source, the corrections of nonlinearity for low energy electrons being made according to Taylor's results.<sup>8</sup> Scintillator and photomultiplier are placed in an iron castle 10 cm thick surrounded by a lead castle 10 cm thick. All measurements are made at room temperature.

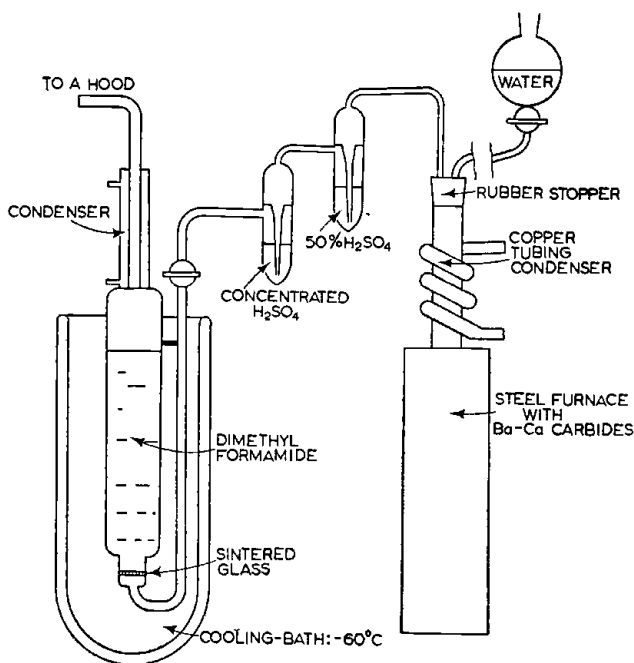


Fig. 3. Furnace for the preparation of  $\text{C}_2\text{Ca}$  and generation of acetylene.

#### CHEMICAL SYNTHESIS OF PARALDEHYDE

The synthesis of paraldehyde involves first the conversion of barium carbonate into a suitable carbide. Most of previous workers (Table 1) have made use of the action carbon dioxide over lithium or barium metals at high temperature. We thought it simpler to start directly from barium carbonate. For

that purpose magnesium has already been mentioned.<sup>3-6</sup> We made trial experiments with lithium on small quantities but the reaction was so vigorous that we did not try to scale it up. Barium metal has been used on micro-quantities by COX and WARNE<sup>15</sup> however barium metal is not commercially available in powder form. We made use of pure calcium available under form of 1.25-2 mm particles. The reaction  $2\text{CO}_3\text{Ba} + 5 \text{Ca} \longrightarrow \text{C}_2\text{Ca} + 2\text{BaO} + 4\text{CaO}$  is strongly exothermic. We succeeded in carrying it out in the steel furnace pictured in Fig. 3 by heating a mixture of 200 g  $\text{BaCO}_3$  and 200 g calcium under a stream of argon. Once started the reaction is very fast and lasts only a few seconds, the furnace reaches dull red through the energy of reaction. In spite of the rapid stream of argon, a certain amount of calcium nitride is formed which ultimately by action of water gives rise to the formation of ammonia which has to be removed in the following step.

Acetylene is generated in an 90% yield in the apparatus Fig. 3 where it is purified by bubbling through  $\text{H}_2\text{SO}_4$ . An excess of calcium being used in the preparation of calcium carbide, acetylene is diluted by hydrogen which would

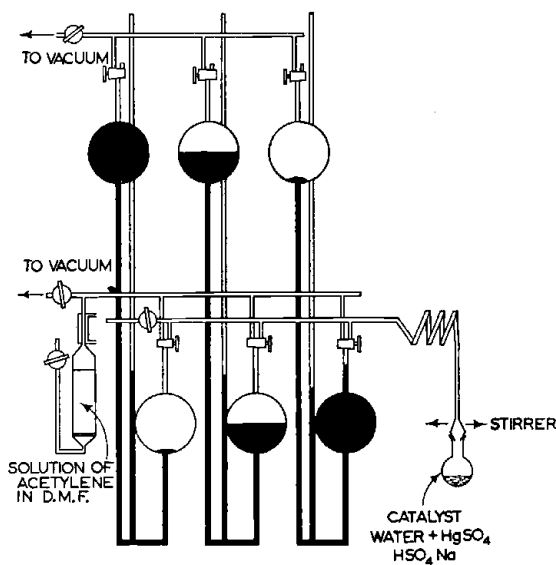


Fig. 4. Apparatus for the preparation of paraldehyde from acetylene.

interfere with the formation of paraldehyde. Hydrogen is removed by dissolving acetylene at low temperature in dimethylformamide DMF; hydrogen being not appreciably soluble in the latter. The flask containing the solution of acetylene in DMF is then attached on the apparatus Fig. 4 where acetylene is slowly evolved by heating, into the containers and then pressed on to Niewland's catalyst: 1 g  $\text{HgSO}_4$ , 20 g  $\text{HSO}_4\text{Na}$ , water: 10 ml.

The absorption of acetylene (12 l. N.T.P.) slow at first, speeds up and requires about 12 hr. The mixture of water and paraldehyde is then vacuum distilled at low temperature and the distillate extracted with 10 ml tetraline, dried over  $\text{Na}_2\text{SO}_4$ , is distilled under 200 mm pressure in an efficient spinning band

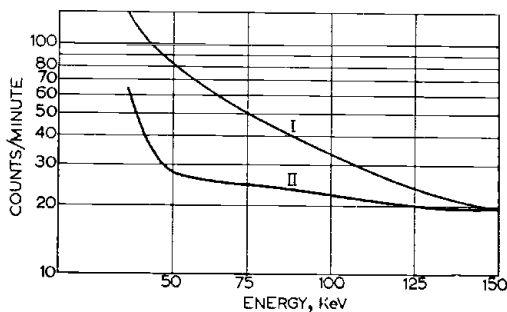


Fig. 5. Integral bias curves obtained for the paraldehyde;  
I modern carbon plus noise.  
II old carbon plus noise.

column. The purity of paraldehyde checked by vapor phase chromatography indicates 1–2% acetaldehyde. Commercial samples of paraldehyde do contain the same percentage. Up to now yield of paraldehyde is about 30%.

#### RESULTS SO FAR OBTAINED

The volume of the scintillator was 20 ml and the concentration of paraldehyde used corresponds to 8 g of carbon to be dated. On Fig. 5 are plotted the integral bias curves for:

- old carbon plus noise (paraldehyde from coal);
- modern carbon plus noise (paraldehyde prepared from ethylalcohol obtained by fermentation).

From these curves the energy band 50–135 keV was selected and the following counting rates were obtained:

- 9.1 counts/min for the 'background';
- 47.8 counts/min for the  $\text{C}^{14}$  of the sample. On a  $4\sigma$  basis and with a counting time of 24 hr samples 38,000 years old can be measured.

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