

PURITY OF BENZENE SYNTHESISED FOR LIQUID
SCINTILLATION C-14 DATING

I. Fraser⁺, H.A. Polach^{*}, R.B. Temple⁺, and R. Gillespie⁺

⁺ The University of Sydney
Department of Physical Chemistry
Sydney, Australia

^{*} The Australian National University
Radiocarbon Dating Laboratory
Canberra, Australia

Abstract

Radiocarbon dating laboratories using the liquid scintillation counting technique synthesise benzene by trimerization of acetylene over commercially available vanadium or chromium activated cracking catalysts. The purity (i.e. absence of quenching agents) of the synthesised benzene is one of the significant factors influencing the reproducibility of C-14 age determinations. However, a recent study has revealed that two laboratories, using the same catalyst and the same synthesis procedures, can obtain a significantly and apparently systematically different level of benzene purity. To evaluate the significance of this we have now analysed the purity of benzene prepared for routine dating by seven established radiocarbon dating laboratories, whose synthesis techniques vary considerably in procedural detail and four of whom use a different type of catalyst.

Generally, the results indicate the presence of the same impurities at approximately the same concentrations in all samples analysed. Acetaldehyde, acetone, butane, ethanol, ethylbenzene, hexane and toluene were identified by gas liquid chromatography as the main impurities present; it could be established that these impurities

(varying in concentration from <20 ppm to <400 ppm) arise, in our own samples, entirely from the acetylene synthesis step preceding benzene catalysts. Of the impurities identified, only acetone appeared in one of the samples analysed in quantities sufficient to be considered a quenching agent. Quantitative experiments were hence carried out to determine its quenching effect at typical equipment settings used for radiocarbon age determinations.

Introduction

The efficient application of the liquid scintillation counting technique to radiocarbon dating requires the quantitative chemical conversion of specimen carbon to liquid scintillant carbon. Whilst a number of procedures were investigated and reviewed by Arnold (1), the most elegant and today the predominantly used technique is based on the conversion of specimen carbon to carbon dioxide (De Vries,(2), Rafter,(3)),with subsequent production of acetylene (Barker,(4)) and polymerization of acetylene to benzene (Noakes et al (5)).

Developments and improvements to the acetylene and benzene synthesis steps (Noakes et al (6), Polach and Stipp(7)) lead to a conversion efficiency of $97 \pm 2\%$ from specimen to benzene carbon. This, coupled with increasing availability of improved commercial liquid scintillation spectrometers, made the technique as used today very attractive. Its evolution and the establishment of low-level liquid scintillation counting for ^{14}C and ^3H age determinations are however based on the efforts of many other researchers, e.g. Tamers et al (9), Starik et al(9), Pietig and Scharpenseel (10), McDowell and Ryan (11), Tamers (12), Polach (13), and others.

Purity of Benzene

It was recognised by all of the workers cited above that it is essential for the synthesised benzene to be highly pure, and procedures such as external standardization (Higashimura et al (14)) and the more common channel-ratio analysis were used, often together in order to detect possible quenching. However, Noakes et al (6) made an attempt to analyse the purity of synthesised

LIQUID SCINTILLATION COUNTING

benzene, and identified acetone as primary contaminant of their experimental samples, with water and ethyl benzene present in trace amounts. They considered that the acetone originated in the cylinder acetylene used for their experiments (acetylene is stored, dissolved in acetone and adsorbed on charcoal), and that it was not a product of the synthesis. They further established that the ethyl benzene was associated with low benzene yields and was present in undetectable amounts when benzene yield approached 90%.

In a recent study, however, Polach et al (15) drew attention to the possible presence of impurities in the synthesised benzene which could cause severe quenching of fluorescence if used for liquid scintillation counting. It seemed particularly significant that following the same synthesis procedures one researcher could obtain reproducibility ultra-pure benzene samples, whilst another researcher consistently obtained samples which contained ethane, butane, acetaldehyde, acetone, ethanol, cyclohexane, toluene, etc., often at significant levels (100 to 400 ppm). As mass spectrometric determinations of the acetylene used for the benzene synthesis indicated that it was always of equally high purity, these results were taken to indicate that minor differences in operating procedures may affect the purity of the sample benzene significantly.

Experimental Methods

In order to study the effect of synthesis procedures in the benzene purity better we have analysed samples prepared for us according to their own normal procedures by the following established radiocarbon dating laboratories: Australian Atomic Energy Commission (Calf); Australian National University (Polach); The British Museum (Burleigh); Illinois Geological Survey (Coleman); University of Bonn (Scharpenseel); University of Sydney (Gillespie); Washington Geological Survey (Pearson).

The samples were examined by gas-liquid chromatography using Pye Series 104 equipment specially fitted with a 50 m capillary column containing poly-propylene glycol. This was operated at temperatures between 60 and 125°C.

A few samples were also examined with a Perkin-Elmer Series 800 ambient temperature instrument using a 3 m column packed with pure Al_2O_3 .

The latter gave much better resolution for lower hydrocarbons, i.e. ethane butane etc. but at the expense of greatly increased scanning time. All impurity levels were determined by comparison with standard samples. Several other types of column were tried unsuccessfully.

Results and Discussion

The results of the current analysis are presented in Table I.

The major impurities identified are ethane, butane, acetaldehyde, acetone, ethanol, hexane, cyclohexane, toluene, and ethylbenzene. These were present essentially at the same concentrations in the Gillespie and Polach samples, and in slightly reduced amounts in the Burleigh samples. The others show a notable absence of ethane, butane, acetaldehyde and hexane; the Calf sample contained no ethyl benzene; the Pearson sample contained no acetone, and the Scharpenseel sample contained significantly more of unidentified product 'X', which appears from mass spectra to be either propene or acetonitrile.

None of the samples, in contrast to the previous study referred to (Polach *et al* (15)), were ultra pure*. It is obviously significant that the new preparations have essentially all those impurities that were present in the original determinations of the Gillespie samples. As among those who submitted samples for analysis, Calf is the only other researcher who uses exactly the same synthesis technique as Gillespie and Polach, we expected his samples to contain either none of the impurities

* 18 purity analyses on benzene residues, as used for dating by Polach, were carried out; only two had toluene at 20-40 ppm concentration; the others were ultra pure, only the benzene peak being present.

LIQUID SCINTILLATION COUNTING

(as obtained previously by Polach, see footnote), or the same level of impurities, as obtained now by both Gillespie and Polach. The fact that the Calf samples showed an immediate level of impurities closely related to the Burleigh, Coleman, Pearson and Scharpenseel samples (all of whom use different catalysts and procedures)** is interpreted by us as indicating that neither the synthesis procedures nor the catalyst used affect the level of benzene sample purity very much.

One common factor in the three sets of samples containing high levels of impurity is that they were freshly prepared for this analysis: whilst the other four sets may also have been prepared freshly, their common characteristic is absence of volatiles. This was thought to be particularly significant and an impure sample was allowed to stand at room temperature sealed in a screw top vial for 2 days and then reanalysed; all impurities except toluene and ethylbenzene were lost. If stored in a refrigerator at ca 3°C the impurities were lost more slowly (up to 14 days) and when frozen in a deep freeze the sample appeared to retain its impurities. It therefore seems likely that the apparent levels of purity reflect conditions of aeration during encapsulation rather than differences in carrying out the benzene synthesis.

To check origins of impurities two further experiments were carried out.

Cylinder acetylene whose purity was established by gas-chromatography was used, and the conditions of benzene synthesis and regeneration of the Noakes' catalyst (i.e. pressure, time, cooling, flushing with dry air, moist air, no flushing) were varied. The resulting benzene purity analysis indicated only the presence of traces of toluene, ethanol and ethylbenzene, confirming Noakes' conclusions

** Calf, Gillespie and Polach used vanadium-activated silica/alumina catalyst supplied by Noakes. Burleigh used ICI cracking catalyst. Coleman used Vanadium activated cracking catalyst No.V-0701 T $\frac{1}{8}$ " supplied by Harshaw Chemicals. Scharpenseel used chromium activated "catalysator-Neu" supplied by Nienburgh-Weser, Hanover.

that if pure acetylene is used, the synthesis products do not contain acetone. However ethanol may also act as a quenching agent if present in sufficient concentration.

The acetylene generated by hydrogenation of lithium carbide was then re-analysed. This confirmed the difficulty in establishing mass spectrometrically the presence of impurities in the acetylene gas at the levels they naturally occur in our samples. However, as it is clearly established in the foregoing that the impurities are carried in the acetylene, the careful purification of acetylene must remain an essential part of the synthesis procedures and the doubts expressed as to its needs and merit by Polach *et al* (15) are no longer valid.

In the quantities found to be present, acetone was thought to be the only impurity which might be capable of producing detectable quenching.

To measure the quenching effect for concentrations of acetone observed (*i.e.* 0-180 ppm), aliquots of acetone were added to a counting sample spiked with ^{14}C to ca. 3000 c.p.m. Table II lists the results.

For a level of 100 ppm of acetone the effect was nil, and only ca 0.2% for the 150 ppm level. This is detectable at count rates of 3000 c.p.m. but at count rates of 30 c.p.m. (*i.e.* modern C^{14} standard value) and less, it would be fully masked by statistical variations. The merit of operating at the balance-point as suggested by Arnold(16) and applied to low-level counting by Leger and Tamers(17) and Polach(13), is clearly seen, as little change in count rate is observed due to the spectral shift due to quenching.

A value as high as 250 ppm of acetone was never observed in any of the samples tested and whilst its effects might be significant they need not be considered. Should such a level of contamination however occur, the associated significant change in channel-ratio or external standardization count rate would warn of its presence.

LIQUID SCINTILLATION COUNTING

Conclusions

The conditions used for benzene synthesis and the type of cracking catalyst used do not affect the purity of benzene synthesised from acetylene. With the exception of toluene and ethylbenzene and traces of ethanol, no impurities are formed during the polymerization step if pure acetylene is used for the benzene synthesis. It is therefore concluded that these are present in the acetylene generated from the lithium carbide by hydrolysis and the acetylene purification step must not only be retained but possibly should be improved.

The impurities are volatile; aeration of produced benzene reduces the levels of impurities to negligible proportions. Should however by accident the impurities attain a >150 ppm level, then their effect might become significant if not detected by channel ratio or external standardization analysis.

Acknowledgements

We wish to thank all those colleagues who made synthesised benzene available for analysis.

References

1. J.R. Arnold, in Liquid Scintillation Counting, p.129 (C.G. Bell and F.N. Hayes Eds.), Pergamon Press (1958).
2. H.L. De Vries, Appl. Sci. Res. Section B, 5, 387 (1955).
3. T.A. Rafter, New Zealand J. of Science and Technology, Section B, 36, 363 (1954).
4. H. Barker, Nature, 172, 631 (1953).
5. J.E. Noakes, A.F. Isbell and J.J. Stipp, Geochim. Cosmochim Acta, 27/7, 797 (1963)
6. J.E. Noakes, S.M. Kim and J.J. Stipp, Radiocarbon and Tritium Dating Proceedings VI Internatl.

6. (Continued)
Conf. Pullman, Washington (1965).
7. H.A. Polach and J.J. Stipp, *Internatl. J. Appl. Rad. Isotopes*, 18, 359 (1967).
8. M.A. Tamers, R. Bibron and G. Delibrias, *in Tritium in the Physical and Biological Sciences*, I.A.F.A., Vienna, 1, 303 (1962).
9. I.E. Starik, K.A. Arslonov and I.R. Klener, *Radiochimiya*, 5, (1963).
10. F. Pietig and H.W. Scharpenseel, *Atompraxis*, 10, 71, (1964).
11. L.L. McDowell and M.E. Ryan, *Radiocarbon* 7, 174 (1965)
12. M.A. Tamers, *Radiocarbon and Tritium Dating Proceedings VI*, *Internatl. Conf. Pullman Washington*, 53 (1965).
13. H.A. Polach, *Atomic Energy in Australia*, 12, 21, (1969)
14. T. Hagishimura, O. Yamada, N. Nohara and T. Shider, *J. Appl. Rad. Isotopes*, 13, 308 (1962).
15. H.A. Polach, J. Gower and I. Fraser, *8th Internatl. Conf. on Radiocarbon Dating*, Lower Hutt, New Zealand, 144, (1972).
16. J.R. Arnold, *Science*, 119, 155 (1954).
17. C. Leger and M.A. Tamers, *J. Appl. Rad. Isotopes*, 15, 697 (1967)

LIQUID SCINTILLATION COUNTING

TABLE I

Major Impurities in benzene
samples in ppm

	A	B	C	D	E	F	G
Ethane	120- 400	150 -350	0- 100				
Butane	20- 70	25- 60	0- 30				
Acetal- dehyde	0- 30	~10					
Acetone	20- 180	105- 130	0- 20	0- 40	0- 30		45
Ethanol	0- 40	0- 10	0- 40		~10	~10	
Hexane	0- 80	60- 70	0- 20	0- 20			
"X"	0- 3	2- 5	0- 6				80
Cyclohexane	0- 100	80- 90	0- 370	0- 50		~20	
Toluene	40- 950	60- 100	400- 1100	20- 800	20- 50	~95	600
Ethyl- benzene	0- 250	30- 40	120- 180	60- 120		~80	70
No. of Samples	30	2	3	6	3	1	1

A. Gillespie
B. Polach
C. Burleigh

D. Coleman
E. Calf
F. Pearson

G. Scharpenseel

TABLE II

Effect of Acetone quenching on
sample countrate

Acetone ppm	Decrease in countrate
0	0 ^b
50	0 ^b
100	0 ^b
150	0.2% ^a
250	0.5% ^a

- a. Mean of 2 determinations individually prepared.
- b. Mean of 4 determinations individually prepared.

Sample counting times \sim 3000 cpm and
individual sample counting times were
c.a. 60 minutes.