

BENZENE PURITY IN RADIOCARBON DATING SAMPLES

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ABSTRACT. Gas chromatographic analysis of the benzene obtained for radiocarbon dating revealed only very low levels (<200 ppm in total) of impurities, most of which were alkylbenzenes. Traces of acetone and phenol were also found. These impurities, at such low levels are thought unlikely to affect counting efficiency.

INTRODUCTION

Cyclotrimerization of acetylene to produce benzene for use in liquid scintillation spectrometry is now a common procedure in many radiocarbon dating laboratories. The technique employs commercially available cracking catalysts activated by chromium, vanadium or molybdenum in high valency state. It is important that the benzene synthesized should be of a sufficiently high purity that quenching is minimal so that the age determinations are consistent. Several previous studies of benzene purity have been made (eg, Coleman *et al*, 1973; Polach, Gower & Frazer 1973; Tamers, 1975). These authors all report high yield of benzene but with side products in small quantities including acetone and methanol. It is important that the purity of the benzene synthesized in dating laboratories should be kept under review.

AIMS

The study here outlined was to investigate the level of impurities in benzene synthesized using a chromium-activated cracking catalyst (KC-Perlkator D1) and to check reports of non-catalytic redox reactions leading to the incorporation of oxygen and the formation of acetone and possibly other oxygen-containing products.

METHODS AND RESULTS

Specimens of benzene for analysis were obtained from separate ^{14}C samples, which included peat, soil, marine silt and bone collagen. In each case fresh catalyst was used to prepare the specimens of benzene. The catalyst was heated for several hours in air and dried thoroughly by heating in vacuum before use. The isolated yield of benzene in each of the runs was 90-100%. Analyses of the benzene were carried out on a Hewlett-Packard 5890 gas chromatograph linked to a mass spectrometer detector. A methyl silicone capillary column (length 12m, id 0.2mm) was used with a temperature program of 40°-100°C in 5 min, a split ratio of 7.5 and a carrier gas (helium) flow rate of 0.88ml/min. The components were identified from their mass spectra and by co-injection with authentic samples. The amount of each component was determined using a series of separately prepared standard solutions together with values of chromatographic peak areas. The analytical results showed that all the samples consisted of benzene in a high state of purity (>99.9%). Each specimen of benzene was found to contain

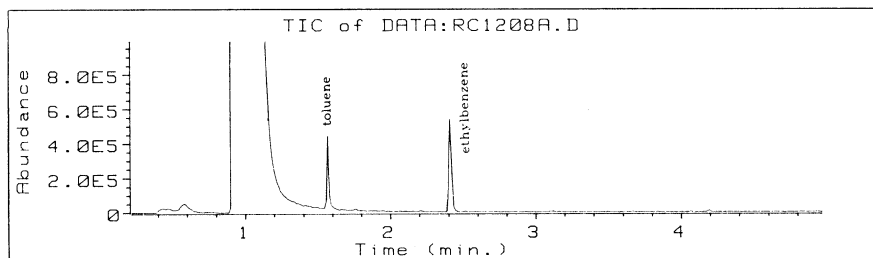
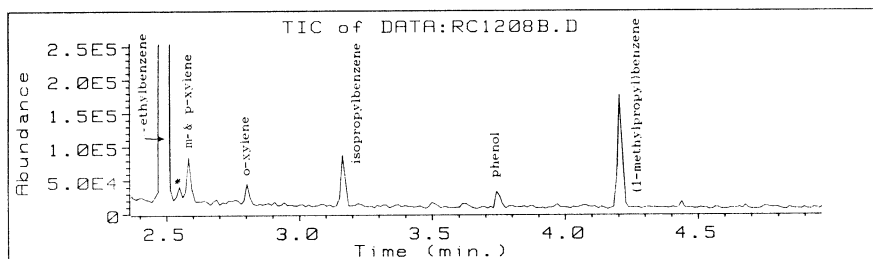


Fig 1. Total ion chromatograph of sample RC 1208



* Impurity from column

Fig 2. Total ion chromatograph of sample RC 1208 at high sensitivity

TABLE 1
Impurities in benzene specimen RC1208

Component	Retention time/min	Quantity	
		Relative abundance	ppm
Benzene	0.997	100	—
Ethylbenzene	2.495	8.6×10^{-3}	86
Toluene	1.566	6.0×10^{-3}	60
Acetone	0.575	7.2×10^{-4}	7.2
(1-methylpropyl)benzene	4.203	3.8×10^{-4}	3.8
Isopropylbenzene	3.163	1.6×10^{-4}	1.6
<i>m</i> -Xylene & <i>p</i> -Xylene*	2.582	1.4×10^{-4}	1.4
<i>o</i> -Xylene	2.802	6.3×10^{-5}	0.6
Phenol	3.742	5.2×10^{-5}	0.5

**m* & *p* xylenes could not be separated effectively on the column used

the same nine impurities: – ethylbenzene; toluene; acetone; (1-methylpropyl)benzene; isopropylbenzene; ortho, meta and para xylenes and phenol. The concentrations of these impurities varied haphazardly between specimens up to 30% or more. The reasons for these variations is unknown, but considering that the benzene was obtained from different types of ^{14}C samples, it is perhaps not too surprising. Chromatographs for sample RC1208, which was considered to be a typical sample, are shown in Figures 1 and 2 with corresponding analytical data in Table 1. The amount of ethylbenzene in RC1208 was towards the top of the range; values from other specimens were generally ca 60 – 70 ppm. For comparison, levels of impurities in scintillator-grade benzene (ex BDH) are shown in Table 2.

TABLE 2
Impurities in scintillator-grade benzene

	Concentration ppm
Toluene	6.0
Ethylbenzene	2.8
<i>m</i> + <i>p</i> xylene	3.6
Methylcyclohexane	3.0
Methylcyclopentane	3.0
Chloroform	0.6

DISCUSSION

The results clearly demonstrate the high level of purity of the benzene. Most of the side products are alkylbenzenes, with toluene and ethylbenzene as the major contributors. Similar findings were obtained by Polach (1973) using the Noakes vanadium catalyst. The origin of these alkylbenzenes is uncertain. Shirakawa and Ikeda (1974) reported the formation of small amounts of ethylbenzene during the cyclotrimerization of acetylene on a tris(acetylacetonato)titanium(iii)-diethylaluminium chloride catalyst. They argued that the ethyl group was derived from the catalyst. With our catalyst, such an explanation is not possible. It may be that the formation, in our system, of both ethylbenzene and (1-methylpropyl)benzene involves hydrogen transfer reactions from other acetylene molecules. Such loss of hydrogen from acetylene has been reported by Tamers (1975). Alternatively, residual traces of water in the catalyst could be involved, despite the latter being carefully heated *in vacuo* before use. It is very difficult, if not impossible in practice to remove the last vestiges of water from so porous a material. The presence of toluene, xylenes and isopropylbenzene could be explained by the presence of propylene in the acetylene. Further work is needed to clarify these points.

The low levels of acetone and phenol indicate some incorporation of oxygen from the catalyst or from traces of water into the non-volatile products. Both this and reactions involving hydrogen transfer suggest that some non-catalytic redox reactions take place on the catalyst. That such reactions

occur is confirmed by the color change of the catalyst during reaction (typically from yellow to greenish gray to brown). The possible formation of non-volatile products, which might also contain oxygen, such as polymers (Belluomini *et al*, 1978) and acetates and carbonates (Tamers, 1975), was not investigated in this study; however, the non-quantitative yields of benzene from some of the runs suggest that non-volatile products are indeed formed. Table 2 shows that the level of impurities in scintillator-grade benzene are considerably lower than in that synthesized from the ^{14}C samples. The type of impurities, however, are similar, with the exception of chloroform. This is an unexpected contaminant, but the concentration is very low and it is most unlikely to affect the counting efficiency.

Although several impurity compounds are present in the benzene synthesized from ^{14}C samples, their levels are low and it is likely that they present no problems in dating. However, further investigations are planned to attempt to account for the formation of these compounds and to discover at what concentrations some or all of them might become significant in age determinations.

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