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Gas Chromatographic Determination of Pentachlorophenol in Human Blood and Urine

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The extraction, identification and quantification of pentachlorophenol (PCP) in human blood and urine are of great importance for monitoring human exposure to this environmental chemical. The wide spread use of PCP in agriculture, industry and households, combined with its highly toxic and rather stable nature, has generated the need to establish the extent of its storage in human body and its fate in the environment. Although reports abound in the literature on PCP residues, toxicity and environmental fate (Bevenue and Beckman 1967; Shafik 1973; Ohe 1979; Rivers 1972), there is hardly any information on its existence in the developing tropical countries, particularly in Nigeria. There is therefore the need to survey the status of PCP in Nigerian environment with a view to establishing the potential health hazards resulting from its bioaccumulation. This paper reports a preliminary survey of the residue levels of PCP in human blood and urine of the general population in Bendel State of Nigeria.

MATERIALS AND METHODS

A Varian 3700 gas chromatograph equipped with ^{63}Ni electron capture detector, and a 25m x 0.25mm glass capillary column coated with SE 54 was used. The operating conditions were: injector temperature, 220°C; detector, 320°C; column, 160°C; nitrogen flow rate 4 ml/min.

All solvents were of pesticide quality and all other reagents were analar grade. The PCP standard was provided by Professor Sören Jensen of University of Stockholm, Sweden.

The modified procedure employed here represents a combination of features taken from methods described by Chau and Coburn (1974) and Edgerton and Moseman

(1979). 2 ml of urine acidified with 0.5 ml concentrated hydrochloric acid was placed on water bath at 80°C for 1 hour. After cooling to room temperature, the sample was extracted thrice with 5-ml portions of hexane/diethyl ether mixture (1:1). The combined organic phase was reduced to about 4 ml by a stream of dry nitrogen. Then 2 ml 0.5M NaOH was added and after shaking for two minutes and centrifugation, the organic phase was discarded. The PCP, now in the aqueous alkaline phase, was acetylated by adding 2 ml 2M K_2HPO_4 2 ml hexane, 25 µl pyridine and 10 µl acetic anhydride. The mixture was shaken for one minute and after centrifugation, the organic phase was now ready for gas chromatograohic analysis.

About 10 ml of blood was collectd in a heparinized tube from each donor. After centrifugation at 4000 rpm for 20 minutes, 2g of the upper serum layer was taken and combined with 2 ml formic acid and 1 ml hexane. This mixture was placed in a water bath at 80°C for one hour with occasional shaking. After cooling and centrifugation, the aqueous phase was further extracted with 2 ml hexane/diethyl ether mixture (2:1). The combined organic phase was now treated as in the previous paragraph.

Routine procedural blanks were run concurrently with the various samples. Quantitation was accomplished by comparison of peak height measurements obtained from both the sample and the standard.

RESULTS AND DISCUSSION

The analyses were made with 35 urine samples and 29 blood samples. Each sample lot was taken from individuals who were either related or living under identical or similar conditions. All individuals were occupationally unexposed. The acetyl derivatives of PCP were preferred to the methyl ether derivatives because of their better gas chromatographic properties. Coutts et al. (1979) demonstrated that excess acetic anhydride in the acetylation procedure did not interfere with the quantification of the PCP acetate while Rivers et al. (1970) reported that interfering responses could be encounted with the use of diazomethane solution due to impurities in the reagent.

Confirmation of PCP was done in accordance with the method described by Erney (1978). Both standard and sample solutions used for gas chromatographic quantitation were simultaneously exposed to UV irradiation and characteristic photodecomposition patterns were obtained. Identical photodecomposition patterns conf-

Table 1. Levels of Pentachlorophenol in Blood and Urine of Nigerian general population

Sample Code	Number analysed	Average level in urine(ppm)	Average level in blood(ppb)
AU	2	0.048	-
AU_2	3	0.025	4.09
AU_3	2	0.23	21.33
CU	4	0.14	15.28
DU	3	0.081	7.97
FU	2	0.097	-
CU_1	1	0.041	6.88
S_1U	4	0.056	-
S_2U	4	0.048	7.10
UU	4	0.17	18.31
V_1U	3	0.21	-
YX_1	3	-	10.20
YX_2	2	-	14.36
V_2U	3	0.11	17.64

irmed the identity of PCP.

Table 1 contains both the blood and urine levels of PCP for the 40 participants included in this investigation. PCP was identified in all samples analysed. The average levels obtained for each sample lot ranged from 0.025 - 0.23 ppm for urine and from TRACE to 21.33 ppb for blood. These values are significantly lower than those reported for citizens in Hawaii (Bevenue et al. 1968; Rivers 1972) and in Florida (Morgade et al. 1980). The amounts in urine were, as expected, generally greater than those in blood which could be indicative of a high rate of PCP excretion in human beings. Owing to this excretion rate the urine

system often provides a convenient monitor for PCP exposure.

It would appear that even with the widespread use of PCP in the environment, the origin of its residue in humans is still not well understood (Ohe 1979). It has been suggested that PCP is one of metabolites of hexachlorobenzene (HCB) or gamma-HCH (Engst et al. 1976). Since gamma-HCH is still very much used in Nigeria, its contribution to PCP storage in Nigerian human population may not be ruled out. Nevertheless, on the basis of the levels obtained in this study, it could be concluded that humans, even in areas like Nigeria, where PCP is not heavily in use, are continously exposed to low levels of this chemical from the environment. Though these findings may not be considered to be toxicologically significant, the possibility of toxicological effects from continued exposure cannot be overemphasized. Therefore further investigations into the possible effects of PCP pollution of the Nigerian environment are necessary. Also its bioaccumulation in adipose tissues, for example, should be studied in relation to the excretion levels.

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