

In 1920 Delgado Palacios (11) found these same waters to contain 784.8 ppm of total salts, and Wieder (12) found a total salt concentration of 931-945 ppm a few years later (1939). From these data it is possible to construct the curve shown in Fig. 1.

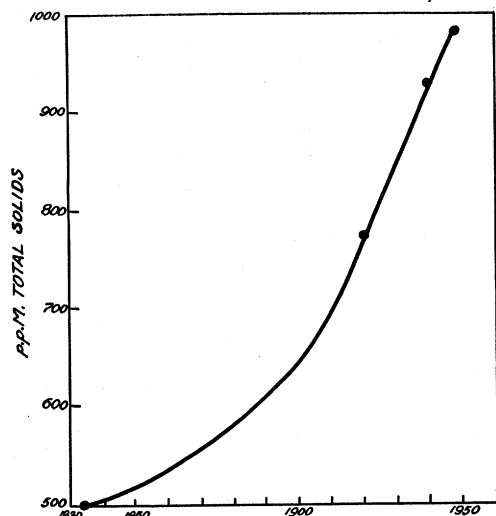


FIG. 1.

In an attempt to locate the origin of these large salt concentrations, Bonazzi in 1948 submitted the waters of a number of tributary streams to analysis. Sampling was left for the driest period of the year (March), since at that time the salt content of the waters logically should be at its highest. Many of the smaller tributaries were dry, so that sampling was done only of the rivers mentioned in Table 2, above the place where there could

TABLE 2
ANALYSES OF TRIBUTARY STREAMS, 1947 AND 1948

		Sampling localities				
		R. Guigüe	Station 6	R. Guayos	R. Delicias	R. Aragua
Silica	SiO ₂	0.0	0.0	6.20	1.20	9.2
Alumina	Al ₂ O ₃	0.0	0.0	1.38	—	0.84
Total iron	Fe ₂ O ₃	—	—	4.82	5.28	8.36
Calcium	CaO	41.48	61.02	96.06	6.18	104.00
Magnesium	MgO	8.90	15.60	12.60	2.00	13.80
Sulphates	SO ₄	19.00	46.50	31.80	3.40	41.70
Chlorides	Cl	4.83	12.07	7.24	4.83	6.04
Total solids, ppm		74.0	173.5	149.0	32.0	161.0

be a possibility of contamination from salts previously deposited in the lowlands or where the rivers might be passing through a salty area.

From the foregoing it is evident that the total salt concentration of the tributary streams today fluctuates around 118 ppm, the SO₄ around 28.5 ppm, and the Cl around 7.0 ppm.

The values presented in this paper may explain the mechanism of salinification of many agricultural soils of

the valley of Aragua, which in some extreme cases have been found to contain 11,150 ppm of Cl and 28,604 ppm of SO₄. Evidently this process was already in progress in the early part of the 19th century and has recently become intensified.

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The Synthesis of 1,1,1-Trichloro-2,2-bis-(4'-Chlorophenyl-4'-C¹⁴)-ethane

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In order to make available for tracer studies samples of the potent insecticide DDT [1,1,1-trichloro-2,2-bis-(4'-chlorophenyl)-ethane], we undertook the synthesis of this compound labeled in the benzene rings with carbon 14. Since both benzene-1-C¹⁴ (1) and aniline-1-C¹⁴ (2) are readily accessible, we investigated the preparation of tagged chlorobenzene by direct chlorination of benzene, as well as by the Sandmeyer reaction with aniline.

When chlorine is allowed to react with an excess of benzene in the presence of suitable catalysts such as aluminum turnings or iron and iodine, chlorobenzene is obtained in 80-90% yield based on the benzene actually consumed, and the formation of more highly chlorinated derivatives occurs to only a limited extent (3, 4). In the presence of an iron-iodine catalyst in a sealed tube at temperatures from 0° to 30°, the reaction of equimolar quantities of benzene and chlorine afforded chlorobenzene in yields ranging from 42 to 65%, together with unreacted benzene and considerable quantities of dichlorobenzene and resin.

The preparation of chlorobenzene was most satisfactorily achieved by reaction of benzene diazonium chloride with hot cuprous chloride solution (5). This procedure afforded pure chlorobenzene in 68-75% over-all yield from aniline, and is of particular advantage in the small-scale preparation of the labeled halide, since it yields a uniquely labeled derivative, and avoids the necessity of

separating the product from more highly chlorinated material.

The reaction of chlorobenzene and chloral hydrate in the presence of various condensing agents has been the subject of numerous investigations. With concentrated sulfuric acid, the reaction of chloral with a 10% excess of chlorobenzene afforded *p,p'*-DDT, mp 106.5°–107.5° C, in about 45% yield (6); anhydrous hydrogen fluoride has also been employed, but the yield of pure *p,p'*-DDT by this technique was not reported (7). With chlorosulfonic acid, Cook and co-workers obtained *p,p'*-DDT, mp 104°–105° C, in approximately 62% yield (8); under similar conditions we obtained pure *p,p'*-DDT, mp 108.5°–109.5° C, in yields that ranged from 40–50% based on chlorobenzene. The substitution of chloral for its hydrate, or the use of 10% excess chlorobenzene, failed to improve the yield of pure material.

PREPARATION OF CHLOROBENZENE

A. *Chlorination with gaseous chlorine.* Generation of known quantities of chlorine was accomplished by the addition of excess concentrated hydrochloric acid solution to potassium permanganate as described by Graebe (9). The apparatus consisted of a generating flask equipped with a gas inlet tube and connected through a pressure-equalizing dropping funnel to a series of 4 gas washing bottles and then to 2 spiral traps attached to a small manifold. Potassium permanganate (254 mg) was placed in the generating flask; after the system had been flushed with a slow stream of nitrogen, the spiral traps were immersed in liquid nitrogen and 18 ml of concentrated hydrochloric acid solution was added slowly to the permanganate. When the vigorous reaction had subsided, the mixture was heated to boiling to complete the generation of chlorine, which was swept with a stream of nitrogen through 1 wash bottle filled with water and 2 containing concentrated sulfuric acid into the liquid nitrogen traps. After 45 min the spiral traps and manifold were isolated from the generating system and evacuated to 10^{-8} mm. By distillation of the product into an excess of alkali, and titration with standard thio-sulfate solution, the yield of chlorine was estimated to be 90% of that calculated from the permanganate employed.

Under high vacuum 38.9 millimoles of dry chlorine was distilled into a 500-ml rb flask immersed in liquid nitrogen and containing 3.00 g (38.9 mM) of benzene, 30 mg of iodine, and 30 mg of iron wire. The reaction vessel was sealed and immersed in a bath at 0°–2.5° C; after 4 hr in the dark at this temperature, the flask was opened, its contents were dissolved in ether, and the solution was washed with alkali and water. Distillation afforded 2.79 g (65%) of chlorobenzene, bp 125°–135° C, n_D^{26} , 1.5176–1.5242, as well as 1.06 g of higher boiling products.

B. *Sandmeyer reaction.* Aniline hydrochloride, 6.50 g (50 mM) was diazotized at –10° C with nitrous acid. Cuprous chloride, freshly prepared from 15.6 g copper sulfate, was dissolved in 22 ml of concentrated hydrochloric acid solution in a 500-ml 3-neck flask. The reaction vessel was equipped with a mercury-sealed Hershberg stirrer, a pressure-equalizing dropping funnel, and an

efficient condenser, which was connected by means of ground glass joints to a trap immersed in liquid nitrogen. The solution of cold diazonium salt was transferred to the dropping funnel and added at a moderate rate to the hot solution of cuprous chloride. A rapid evolution of nitrogen began immediately; stirring was continued with no external heating for 15 min after the addition was complete. The reaction mixture was extracted with ether, and the flask and condenser were rinsed with ether to recover droplets of chlorobenzene carried into the condensing system by the rapid evolution of nitrogen. The ether extracts, washed with alkali and water, were dried over calcium chloride. Distillation afforded 4.12 g (73%) of chlorobenzene, bp 125°–129.5° C; $n_D^{26.5}$, 1.5198.

1,1,1-TRICHLORO-2,2-BIS-(4'-CHLOROPHENYL)-ETHANE

A 100-ml 3-neck rb flask was equipped with a mercury-sealed Hershberg stirrer, a drying tube filled with potassium hydroxide, and a pressure-equalizing dropping funnel prepared from a 5-ml graduated pipette with a capillary tip; 2.98 g (19 mM) of finely ground chloral hydrate, mp 59°–60° C, was dissolved with stirring and warming in 4.05 g (36 mM) of chlorobenzene. When solution was complete, the flask was cooled to 10° C in an ice bath and 2.32 ml (36 mM) of freshly distilled chlorosulfonic acid was added at the rate of 1–2 drops/sec, with vigorous stirring. Addition was complete after about 90 min, during which time the reaction mixture became somewhat dark; the ice bath was removed, and hydrogen chloride was evolved as the mixture slowly came to room temperature. Stirring at room temperature was continued for 20 hr, during which time the product precipitated as a crystalline mass.

After addition of a few ml of ice water, the mixture was extracted with a total of 30–40 ml of carbon tetrachloride; the organic extract was washed with cold water, with 2% sodium carbonate solution, and again with cold water. Concentration of the dry solution in vacuum afforded a colorless oil, which was transferred to a 50-ml centrifuge tube with 15 ml of 95% ethanol. On cooling, crude DDT, mp 97°–102° C, was obtained in yields which varied from 75–85%; a second crystallization from 95% ethanol afforded pure *p,p'*-DDT, mp 108.5°–109.5° C, in over-all yields of 40–50%.

A sample of 1,1,1-trichloro-2,2-bis-(4'-chlorophenyl-4'-C¹⁴)-ethane prepared from chlorobenzene-1-C¹⁴ under the conditions described above had a specific activity of approximately 54 μ c/mM.

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