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A contributive error from analytical reagents in the analysis of chlorophenoxy acids and pentachlorophenol by electron capture gas chromatography

In the analysis of the esters of chlorophenoxy acids, and the ethyl or methyl derivatives of hexachlorophene and pentachlorophenol (PCP) in plant and animal tissue and water samples, it is common practice to employ basic analytical grade reagents for adjustment of the pH of the sample mixture prior to isolation of the desired compound from the sample[1–7]. High purity, analytical grade, chemical reagents

TABLE I

ANALYTICAL GRADE REAGENTS USED IN THIS STUDY

Reagent[a]	*Grams added to 2800 ml water*	*Approximate pH of solution*	*Source of reagent*
KOH[b]	18.3	13	J. T. Baker
NaOH	11.3	13	Matheson, Coleman, Bell
NH_4OH	16.9	11	Mallinckrodt
Na_2CO_3	29.7	11	Matheson, Coleman, Bell
$NaHCO_3$	23.5	8	J. T. Baker
H_2SO_4			DuPont

[a] All reagents were purchased in glass containers.
[b] 86% assay.

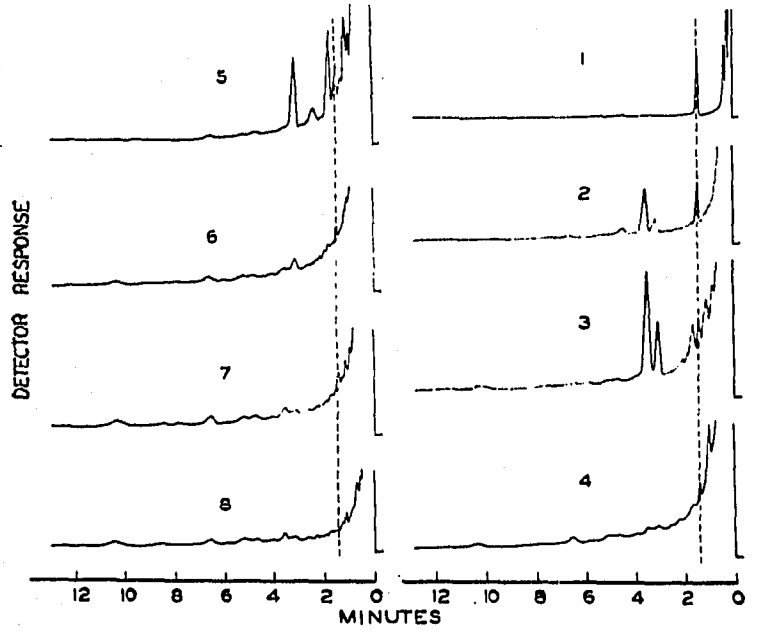

Fig. 1. Gas chromatograph curves obtained from a 1/8 in. × 5 ft. column containing 4% SE-30–6% QF-1 silicones on Chromosorb W-HP, 80–100 mesh. Column temperature 187°; electron capture detector. Curve 1: PCP methyl ether, 60 pg; curve 2: $NaHCO_3$, 3 µl (aliquot from 0.5 ml hexane extract (hexane extract equivalent to the 2800 ml 0.1 *M* reagent solution)); curve 3: Na_2CO_3, 5 µl; curve 4: KOH, 10 µl; curve 5: NaOH, 3 µl; curve 6: NH_4OH, 5 µl; curve 7: H_2O + H_2SO_4 + diazomethane (control), 10 µl; curve 8: H_2O + H_2SO_4, 10 µl.

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may contribute extraneous and additive false data to the final analytical values of the desired compound, as shown below; especially, if analysis is conducted in the parts per billion (p.p.b.) or parts per trillion (p.p.t.) range.

TABLE II

APPARENT PENTACHLOROPHENOL (PCP) IN REAGENTS

Reagent	*Gross PCP (p.p.t.)*	*Net PCP*[a] *(p.p.t.)*
Water + H_2SO_4 (control)	0.22	—
KOH	0.18	—
NaOH	1.10	0.88
NH_4OH	0.31	0.09
Na_2CO_3	0.67	0.45
$NaHCO_3$	1.80	1.58

[a] After deducting water + H_2SO_4 control value.

To simulate the extraction procedure for the analysis of a water sample, solutions of 0.1 *M* of each of the chemicals listed in Table I were prepared with 2800 ml tap water. Each solution was then adjusted to approximately pH 2 with 18 ml concentrated sulfuric acid and extracted with 100 ml redistilled hexane. (All of the glassware used in the experiments were either heat-treated at 200° for 16 h or treated with a solution of concentrated sulfuric acid–potassium dichromate[8].) The hexane extract was concentrated to 0.5 ml and treated with excess diazomethane solution; the excess diazomethane was removed by aeration with nitrogen, the sample was again concentrated to 0.5 ml and aliquots were applied to a gas chromatograph utilizing an electron capture detector. The results are shown in Fig. 1. Table II illustrates the error contributed by the added chemical reagent relative to the analysis of PCP in the picogram range. It is also noted in Fig. 1 that other and larger amounts of extraneous components from some of the reagents could magnify the error or confuse the gas chromatographic data in the analysis of chlorophenoxy acids. The use of potassium hydroxide would be preferable to sodium hydroxide, at least, with the particular commercial reagents used in this study.

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1 M. T. SHAFIK, *161st National Meeting, Amer. Chem. Soc., Los Angeles, Calif., March 28–April 2, 1971*, Abstracts of Papers.
2 G. YIP, *J. Ass. Offic. Anal. Chem.*, 54 (1971) 343.
3 M. CRANMER AND J. FREAL, *Life Sci.*, 9 (1970) 121.
4 P. W. WILLIAMS AND J. I. TEASLEY, *J. Ass. Offic. Anal. Chem.*, 52 (1969) 782.
5 D. G. CROSBY AND J. B. BOWERS, *Bull. Environ. Contam. Toxicol.*, 1 (1966) 104.
6 G. YIP, *J. Ass. Offic. Agric. Chem.*, 47 (1964) 1116.
7 G. YIP, *J. Ass. Offic. Agric. Chem.*, 47 (1964) 343.
8 A. BEVENUE, T. W. KELLEY AND J. W. HYLIN, *J. Chromatogr.*, 54 (1971) 71.

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