

Use of Simple Sets in Isolating Interferences in Analyses of Pesticide Residues

The utility of employing simple sets to isolate troublesome interference in process blanks analyzed by gas-liquid chromatography (GLC) is demon-

strated. A specific example is explained and the value of sets has been suggested for use in other complex analysis problems.

In the course of analyzing pesticide extraction blanks by gas-liquid chromatography (GLC), the Iowa Community Pesticide Study Laboratory occasionally encounters complex tracings containing many extraneous peaks. In our experience, these peaks have arisen from artifacts or impurities in the reagents used, and are not pesticide residues. Since these peaks interfere with subsequent sample analysis, it is imperative that the responsible reagents be identified and purified. Often one or more of the reagents are known to be free from contamination, thereby greatly simplifying the search for the impure reagent.

One way to locate the problem reagent is to test the reagents singly when possible. In the case of some hydrocarbons and other low-boiling organic liquids, this is easily done by reducing the volume several hundred-fold and analyzing the residue by GLC in an appropriate solvent. However, this approach is neither always economical nor possible. It is precluded in the case of salts, drying agents, chromatographic substrates, high boiling ethers, polyhydric alcohols, and other GLC-refractory materials which may be used in the pesticide extraction process. These substances must nearly always be analyzed in combination after being exposed to solvents, which may themselves be suspect.

This communication will attempt to demonstrate how effort can be reduced by considering *any* such combinations as sets which can be subtracted. In this manner impure reagents can be quickly isolated, several at a time.

PROCEDURE

A process reagent blank was desired for a pesticide residue technique applicable to air sampling. The method chosen for the analysis was that of Stanley (1968). This is a process whereby a solid adsorbant (alumina) in a scrubber tube and propylene glycol in an impinger are mounted in tandem in an air sampling device. Following sample collection, the media are extracted with methanol and hexane, respectively. The combined extract is then eluted from a Florisil column with solutions of dioxane in hexane.

The blank for the entire method was obtained by following the procedure as written. Glass distilled hexane and methanol were purchased from Burdick and Jackson, Muskegon, Mich. Activated 80/100 mesh chromatographic grade alumina, reagent grade *p*-dioxane, propylene glycol, and sodium sulfate were purchased from Matheson, Coleman and Bell, Norwood, Ohio.

Our GLC system consisted of a MicroTek MT 220 fitted with two 130-microcurie electron capture detectors and two 6-foot \times 1/4-inch glass U tube columns, one of which contained 4% SE-30 6% QF-1 on Anakrom 80/90 mesh SD support. The other contained 3% stabilized DEGS (Analabs) on Gas Chrom Q 80/100 mesh (Applied Science). Both were used for the analyses.

Analysis of this blank by gas chromatography showed that there were materials present in at least one reagent (possibly more) that chromatographed with retention times similar to the pesticides that were to be detected.

The reagents were grouped according to the combinations found in each stage of the procedure. For convenience these symbols were assigned to each reagent: *p*-dioxane = α ; *n*-hexane = β ; propylene glycol = γ ; sodium sulfate = δ ; methanol = ϵ ; alumina = ζ .

The combinations were: (A) $\alpha\beta$; (B) $\beta\gamma\delta$; (D) $\beta\epsilon\zeta$.

Partial blanks A, B, and D were prepared and analyzed. For ease of tabulation "0" was assigned to a reagent that was acceptable and "1" to a reagent that was unacceptable. For *n* combinations there are 2^n configurations of 1 and 0; thus in this case there were eight permutations. Table I displays the three combinations of reagents, and the eight possible ways that 1 and 0 can be permuted three at a time.

A sufficient condition for Case 1 to have arisen would have been $\beta = 1$. It isn't a necessary condition; others sufficient to cause the problem would be: $\alpha.\delta.\zeta = 1$, $\alpha.\gamma.\zeta = 1$. Had the hexane (β) been contaminated, A, B, and D would have resulted in unsatisfactory partial blanks since β is

Table I. Possible Reagent Combinations

Case	Combinations ^a		
	(A) $\alpha\beta$	(B) $\beta\gamma\delta$	(D) $\beta\epsilon\zeta$
1	1	1	1
2	0	0	0
3	1	1	0
4	1	0	0
5	0	1	1
6	0	0	1
7	1	0	1
8	0	1	0

^a 0 is assigned to a reagent if acceptable, and 1 is assigned if the reagent is unacceptable.

Table II. Resolution of Reagent Combinations

Case	Combination			"possibly" 1	1 "for sure" at least one, and sufficient that $\beta = 1$	"possibly" 0	0 "for sure"
	$\alpha\beta$	$\beta\gamma\delta$	$\beta\epsilon\zeta$				
1	1	1	1	all		$\gamma + \delta + \epsilon + \zeta^a$ or $\alpha + \gamma + \delta + \zeta + \epsilon^b$	none
2	0	0	0	none	none	—	all
3	1	1	0	$\gamma + \delta$	α	$\gamma + \delta$	$\beta \cdot \epsilon \cdot \zeta$
4	1	0	0	—	α	—	$\beta \cdot \gamma \cdot \delta \cdot \epsilon \cdot \zeta$
5	0	1	1	$\gamma + \delta + \epsilon + \zeta$	none	$\gamma + \delta + \epsilon + \zeta$	$\alpha \cdot \beta$
6	0	0	1	$\epsilon + \zeta$	none	$\epsilon + \zeta$	$\alpha \cdot \beta \cdot \gamma \cdot \delta$
7	1	0	1	$\epsilon + \zeta$	α	$\epsilon + \zeta$	$\beta \cdot \gamma \cdot \delta$
8	0	1	0	$\gamma + \delta$	—	$\gamma + \delta$	$\alpha \cdot \beta \cdot \epsilon \cdot \zeta$

^a Only if $\beta = 0$.

^b Only if $\beta = 1$.

Let (+) between two or more letters mean "or."

Let (.) between two or more letters mean "and."

common to all three combinations. Fortunately, previous experience had shown the *n*-hexane to be acceptable.

Case 2 was also discounted since an unsatisfactory total blank had been obtained. This left Cases 3 through 8 as the only possible permutations of 1 and 0 that could have resulted in the problem.

Analysis of partial blanks A, B, and D showed that A and B were unsatisfactory while D yielded no interferences. Examination of Table I shows that Case 3 is the permutation that describes the experimental results. The conclusion drawn at this point was that α was definitely contaminated (β having been eliminated by partial blank D) and that γ and δ might be contaminated.

The propylene glycol had been pre-extracted with hexane prior to use and the sodium sulfate had been shown to be interference-free by other tests. For these reasons attention was focused on the *p*-dioxane (α). Bear in mind, however, that at this point γ and δ had not been eliminated as suspected reagents by experimentation.

Commercial dioxane is known to contain impurities of acetaldehyde, ethylene acetal, and water. The dioxane employed in this study was purified by acid hydrolysis, drying, and distillation, whereupon a GLC analysis of a two hundred-fold concentrate proved to be acceptable. The reagents γ and δ would have to be purified or at least checked if there were no previously knowledge of their purity.

Consequently, a sample of 250 ml. of propylene glycol was extracted with *n*-hexane, and the extract was examined by GLC for interferences. There were none. The sodium sulfate had been used previously in many other tests and produced no GLC interferences. For these reasons the cause of the unacceptable partial reagent blank B was ascribed solely to impurities in the *p*-dioxane. A subsequent total blank confirmed that all the reagents were now acceptable.

The conclusions which may be drawn for each of the conceivable GLC results are tabulated in Table II. For the sake of illustration, all cases were included. Case 3 is presented as if there were no prior knowledge about any reagent.

SUMMARY

In the case presented, the cause of the reagent blank problem was isolated, identified, and solved with five operations.

These five operations were three partial blanks and *p*-dioxane and propylene glycol purified and verified. Had a step-by-step procedure been chosen, eight examinations to determine cause and at least one analysis of purified reagents would have had to be done. Thus, the use of simple sets resulted in a considerable saving of time.

The real advantage of presenting combinations for analysis lies in the fact that the GLC results might have shown that Cases 4, 6, or 8 were the troublesome configurations, thus eliminating four or five reagents as the source of contamination. In addition, previous knowledge of the purity of any reagent further reduces labor. This is an inherent bonus of set groupings.

It is unfortunate that in most methods combinations cannot be prepicked for the maximum of information. The order of extractions necessitates the groupings and therefore the amount of effort involved. Each method and each set of reagents will have its own unique number of combinations and resulting permutations of 0 and 1. In any situation, however, a scientific manipulation of symbols similar to the procedure described can result in a considerable saving of effort.

LITERATURE CITED

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