Gas Chromatography of Phosphine Derived from Zinc Phosphide in Sugarcane

William H. Robison and H. Wayne Hilton*

A rapid, sensitive, and specific gas chromatographic method was developed for the analysis of traces of PH_3 from Zn_3P_2 in sugarcane. The PH_3 liberated by acid was absorbed in toluene and measured relative to reference standards. An average of 41.5% of the available PH_3 reacted irreversibly, in the acid medium, with chopped sugarcane. Grain bait containing Zn_3P_2 as a rodenticide and applied by aircraft over sugarcane fields deposited less than 1% of the total Zn_3P_2 in the leaf axils; rainfall was a major factor in reducing or eliminating residues.

Zinc phosphide, Zn_3P_2, a 1.88% active ingredient on oat groats, used as an aerially-broadcast rodenticide in sugarcane fields, may be expected to liberate phosphine, PH_3, in the mildly acidic conditions of moist soil or on deteriorating bait particles. Although 85% of the grain bait sifts through the leaf canopy to the mat of dead abscised leaves (27%) or to the ground (58%), 15% lodges in the leaf axils at the time of application (Nass *et al.*, 1970). Five pounds of bait per application, and a maximum of four applications during the period from 6 to 21 months of the 2-year crop in Hawaii, deposits 0.36 lb of Zn_3P_2 per acre. At an average acre-yield of about 100 tons of sugarcane, 0.47 ppm of PH_3 could be liberated, 0.07 ppm from the Zn_3P_2 retained in the leaf axils. Most the the applied Zn_3P_2 finds its way to the soil and, since the treatments are made over a period of about a year, rainfall, bait deterioration, slow decomposition of Zn_3P_2, and normal leaf abscission would all be expected to reduce or essentially eliminate the potential residues of PH_3 or Zn_3P_2 remaining in the crop at harvest.

The experiments reported in this paper were designed to assess the actual residues of PH_3 or Zn_3P_2 present in sugarcane from normal and from excessive amounts of bait. The fate of Zn_3P_2 in the soil will be reported separately.

A sensitive rapid method of analysis was needed for PH_3 in sugarcane, either for the adsorbed gas or for PH_3 liberated from occluded Zn_3P_2 by treatment with acid. The colorimetric procedure designed to measure PH_3 derived from aluminum phosphide used for grain fumigation (Bruce *et al.*, 1962; Hazleton Labs, 1968) was modified for Zn_3P_2 in sugarcane and was adequate. However, it required large individual samples (1 kg in size), a great deal of care was necessary to see that water, reagents, and glassware were free of phosphate, and the method was time consuming. Only two samples could conveniently be processed per day. Recoveries of PH_3, though consistent, were low.

A gas chromatographic procedure, with specific detection of the phosphorus moiety as PH_3, proved to be simple, rapid, applicable to 50 g of sample or less, and required no sample cleanup.

The earlier gas chromatographic procedures (Berck, 1965; Dumas, 1964, 1969) were not generally suitable, either because of lack of detection specificity or sensitivity. The flame photometric detector (FPD) in the phosphorus mode offered the most specific and sensitive route to quantitative analysis of PH_3 (Berck *et al.*, 1970). However, in place of the injection of N_2-diluted PH_3 gas, we substituted a solvent system in which PH_3 liberated by acid from Zn_3P_2 was absorbed in toluene. An aliquot of the toluene solution was injected directly onto the gas chromatographic column. (Exactly the same response was obtained from a given amount of PH_3 in toluene as in N_2 gas.) The partitioning behavior of PH_3 between toluene, the sugarcane-aqueous substrate, and the headspace gas above the toluene layer in a closed system was investigated.

A simple generator to prepare small quantities of PH_3 gas from Zn_3P_2 is described.

Experiment Station, Hawaiian Sugar Planters' Association, Honolulu, Hawaii 96822

EXPERIMENTAL

General Procedure. Chopped sugarcane containing small amounts of Zn_3P_2 was placed in a sealed Erlenmeyer flask containing aqueous acid and toluene. The concentration of PH_3 in the toluene layer was determined by injecting an aliquot into the gas chromatograph. Reference standards, without sugarcane but with known amounts of Zn_3P_2 in acid and toluene, prepared in the same manner, served as gas chromatographic standards.

Part of the released PH_3 reacted irreversibly with sugarcane when it was present, requiring recovery corrections. Phosphine remaining in the sealed Erlenmeyer flasks equilibrated between the toluene layer, aqueous acid, and gas headspace. The PH_3 in equilibrium in the toluene layer of the sugarcane samples was measured (with the appropriate corrections for recovery) in comparison with the equilibrated PH_3 in the toluene of the reference standards.

The equilibrium ratios of PH_3 in the toluene, acid, and gas phases of the Erlenmeyer flask system were determined and related to known quantities of PH_3 using absolute standard solutions, both of the gas dissolved in toluene—without other equilibration phases—and of a mixture of the gas in N_2.

Gas Chromatography. A Microtek-MT220 (Tracor Instruments, Inc., Austin, Texas) gas chromatograph was fitted with a flame photometric detector (FPD) and the Melpar optical interference filter which isolates the 526-mμ band for P emission. A 4-ft $\times$ 0.25-in. borosilicate glass column packed with 5% QF-1 on Gas Chrom Q, 80–100 mesh, and heated at an isothermal oven temperature of 40° C separated PH_3 from the solvent. Other parameters were: detector, 140° C; inlet, 220° C; nitrogen carrier gas, 45 ml/min; hydrogen to detector, 50 to 150 ml/min; air to detector, 0 to 35 ml/min; oxygen to detector, 10 to 25 ml/min; attenuation settings were generally $10^4 \times 8$ to $10^4 \times 1$. For amounts of PH_3 at or near the limit of detection, higher gas flow rates to the detector gave better sensitivity, with a greater signal/noise ratio than lower flow rates. The limit of detection of PH_3 was about 20 pg (2×10^{-11} g, 8% full scale) with the instrument. Phosphine and toluene were eluted from the column 20 sec and 3.5 min after injection, respectively. Toluene was

used in preference to benzene or hexane because 10 μl did not blow out the hydrogen flame; reagent grade toluene contained no interfering impurities.

The detector response was linear for amounts of PH_3 against peak height; PH_3 eluted as a sharp peak with no tailing and no detectable area.

Sugarcane Analysis. Sugarcane, about 200 lb, randomly selected from experimental plots and including the adhering leaves, was chopped in a silage chopper fitted with a 10% subsample splitting device. The coarse subsample was frozen in a plastic bag for storage or shipment and then reduced to a fine fibrous mat in a food mill (Hobart Food Cutter, Model 8181-D). Samples of 50.0 g were weighed into 250-ml screw-cap Erlenmeyer flasks fitted with Teflon plastic liners in the caps. (For direct gas or liquid withdrawal, a small hole was bored through the screw cap and a silicone-rubber septum glued to the top of the cap over the hole.) Reagent grade toluene, 50 ml, and 10% v/v H_2SO_4, 25 ml, were added and the flasks quickly sealed. The flasks were shaken vigorously by hand for 1 min, on a reciprocating shaking machine for 1 hr, with enough action to splash the sample about halfway up the sides of the flasks, again by hand for 1 min, and again on the shaker for 1 hr. The time may be varied within certain limits, but must be standardized.

The flasks were tapped on the hand to compact the fiber and rested at a 45° angle to allow the toluene layer to separate. A 10-μl portion of the toluene phase, or less as required to give a PH_3 peak height between 5% (at $10^4 \times 1$ attenuation) and 80% (at $10^4 \times 8$ attenuation, about 1 ng at the higher flow rates) full scale, was withdrawn from the flask and injected into the gas chromatograph. Taking into account the corrections to be described, the sensitivity limit of 20 pg PH_3 corresponded to 0.002 ppm on sugarcane. All analyses were performed at ambient temperatures of 27° to 28° C.

Reference Standards. Dry reagent grade D-glucose, ground to pass a 100-mesh screen, was mixed with zinc phosphide powder to make 3.795% Zn_3P_2 corrected for impurities. No pure sample of Zn_3P_2 was available. Commercial grades contained either 88% or 94%, depending on the source. The corrected reference mixture contained 1.000% available PH_3 when completely hydrolyzed with acid. Serial dilutions of 0.100, 0.010, and 0.001% available PH_3 were prepared by adding the required amount of 100-mesh glucose.

Each of the three dilute mixtures, 50 mg, was placed in a 250-ml screw-cap Erlenmeyer flask with 50 ml of toluene, 25 ml of 10% H_2SO_4, and 40 ml of distilled water, replacing the volume ordinarily occupied by the sugarcane sample. These recovery standards, shaken in the same manner and for the same time as the sugarcane samples, contained the equivalent of 1.00, 0.10, and 0.01 ng of PH_3 for each microliter of toluene present. The gas chromatographic peak heights of the PH_3 in the toluene served as reference points for the sugarcane samples; references were prepared each day that analyses were performed. (NOTE: Repeated sampling of the references should be made through a septum, as repeated opening and closing of the flask released the phosphine in the headspace gas; reequilibration reduced the amount of PH_3 in the toluene.)

Alternatively, it was possible to carry out the same analysis by withdrawing an aliquot of the headspace gas through a septum for direct injection into the gas chromatograph. The concentration of PH_3 in the toluene layer was about twice that in the headspace gas.

Recovery of PH_3 from Zn_3P_2 Added to Sugarcane. Sugarcane samples, 50 g, in Erlenmeyer flasks were fortified with the three Zn_3P_2 mixtures in powdered glucose described above for the reference standards, and processed like the sugarcane samples just described.

Using an average recovery of 58.5%, the amounts of PH_3 present in the toluene from sugarcane samples of unknown Zn_3P_2 content were corrected to within ±10% of the true values by multiplying the ng of equivalent PH_3 measured per μl of sample injected by *100/58.5* or *1.71*.

Reference Standard Ratios of PH_3 in Water, Toluene, and Headspace Gas. A large test tube, fitted with a rubber septum screw-cap top and a side-arm having a Teflon stopcock, was connected through the sidearm to a similar test tube acting as a water reservoir and with the screw-cap off. The apparatus was filled with water and pure PH_3 gas, 20 ml, was introduced by syringe through the septum into the closed tube, displacing 20 ml of water through the open reservoir tube. The reservoir cap was screwed on, and 10 psi pressure was applied to the top of the reservoir through a syringe needle, thus pressurizing the PH_3 tube. The stopcock on the PH_3 tube was closed, disconnected from the reservoir, and the PH_3 tube was refrigerated overnight. The pressure and cooling increase the solubility and ensure saturation. The tube was allowed to come to room temperature, and the stopcock was carefully opened (with the septum cap still sealed) to release pressure and then closed again. Aliquots of the saturated water were diluted with water and injected directly into the gas chromatograph. The concentration of PH_3 in the saturated water was 92 ppm.

The PH_3-saturated water, 8.4 ml, and toluene, 8.4 ml, were placed in a glass tube of 25.2-ml capacity (leaving 8.4 ml of headspace) having septum sealed screw caps at each end. The tube was shaken for 1 hr to equilibrate at ambient temperature; aliquots of each layer showed 3.5% of the PH_3 in water, 17.8% in the air space, and 78.7% in the toluene at 28° C.

The 250-ml Erlenmeyer flasks used for analysis of the reference standards contained (by volume) 26% aqueous acid/54% air space/20% toluene. Using the partitioning ratios for the equal-volume condition to calculate the partitioning ratios expected in the Erlenmeyer, one finds

$$0.26 \times 3.5 = 0.97 \div 26.33 = 0.04$$
$$0.54 \times 17.8 = 9.62 \div 26.33 = 0.36$$
$$0.20 \times 78.7 = 15.74 \div 26.33 = 0.60$$

or 4% in the aqueous phase, 36% in the headspace gas, and 60% in the toluene phase. Direct sampling and gas chromatography of the two latter phases gave the results of Table I in good agreement with the calculated values.

Thus the recovery of PH_3 from the toluene phase of the Erlenmeyer flask reference standards, by calculation, should be about 60% of the total PH_3 present because of distribution of PH_3 in other phases. Direct analysis averaged 60.8%.

Table I. Partitioning of PH_3 Between 50 ml of Toluene and 135 ml of Air in Sealed 250-ml Erlenmeyer Flasks

	PH_3 recovery from Zn_3P_2 (%)[a]	
	0.1 ppm	0.01 ppm
Reference samples		
Toluene	62.9	61.5
Headspace	37.1	38.5
Sugarcane samples		
Toluene	63.1	62.5
Headspace	36.9	37.5

[a] Reported as % of recoverable PH_3.

Sugarcane samples added to the flask removed another 41.5% (average) of the PH_3 compared with the reference standards. As an example, an injection equivalent to 1 ng of an absolute standard giving a peak height of 192 mm showed a peak of 109 mm in the toluene from the Erlenmeyer flask without sugarcane, and 63 mm in the toluene layer when sugarcane was present. The absolute recovery, then, of PH_3 in toluene from Zn_3P_2 in sugarcane, using the present method, was 33%.

Recovery of PH_3 from Zn_3P_2 as a Function of Reaction Time. Sugarcane samples, 50 g, containing Zn_3P_2 mixtures in glucose to yield 1.000-, 0.100-, 0.010-, and 0.001-ppm PH_3 based on 50 ml of toluene, were analyzed with toluene and 25 ml of 10% H_2SO_4 as before in 250-ml Erlenmeyer flasks. Shaking time varied from 0.5 to 2.5 hr; samples were also analyzed after standing for 19 and 96 hr. Reference standards were also prepared and used to correct the recovery values from sugarcane. The results are shown in Table II. From the results, 2 hr was adopted as the optimum time.

Comparison of PH_3 in Equilibrium in the Toluene of the Reference Standards with Absolute Quantities of PH_3. PH_3 IN GAS FORM. A 125-ml borosilicate glass separatory funnel with a Teflon stopcock was modified by sealing a 16-mm o.d. × 100-mm long screw-cap borosilicate glass culture tube to the stopper neck. A 24/40 ⅀ male joint was also modified by attaching a 16-mm o.d. × 100-mm long screw-cap borosilicate glass culture tube to the tubing end.

The outlet tip of the modified 125-ml funnel was connected by an 18-in. section of Tygon tubing to the outlet of an unmodified, unstoppered 250-ml separatory funnel. The two funnels were attached to a ring stand so that each funnel could be raised or lowered easily and turned horizontally. With both stopcocks open, freshly prepared 10% H_2SO_4 at 40° C was added to the funnels with their heights adjusted in such a way that the 125-ml funnel was filled completely to the top of the attached culture tube and the 250-ml funnel was filled no more than 1/3 full.

Zinc phosphide, 1 m*M* (258.06 mg) corrected for its stated impurity, was weighed into a No. 2 gelatin capsule. The capsule was dropped into the warm acid in the 125-ml funnel through the culture tube; the funnel height was adjusted if necessary to exclude air completely; and a septum-containing cap was screwed tightly on the culture tube. The smaller funnel was then turned to a horizontal position during reaction to prevent Zn_3P_2 powder from falling in the tubing. (Both stopcocks *must* be open during reaction as the PH_3 forces acid solution out of the smaller into the larger flask. The larger flask is left unstoppered to maintain atmospheric pressure.)

The gelatin capsule dissolved and reaction occurred at a very moderate rate. At least an hour was needed for complete reaction. The 125-ml funnel was then repositioned vertically. CAUTION: Air must not enter the smaller funnel at any time; pure PH_3 is a serious fire hazard. The PH_3 from 1 m*M* of Zn_3P_2 should occupy about 45 ml; the actual volume collected was 44 ml.

Samples of pure PH_3 were withdrawn through the septum with a gas-tight syringe and diluted in N_2-filled, round-bottomed 1-l. flasks containing a few glass beads and fitted with the septum-capped culture tube blown to the 24/40 joint. The dilution method was essentially that of Berck *et al.* (1970). For 1.0 ppm w/v PH_3, 691.8 μl of PH_3 were required per liter of N_2. The total volume of the dilution flask must be predetermined.

To dispose of surplus pure PH_3 from the generator, the 250-ml funnel was filled with water and connected to a gas scrubber containing saturated bromine water with excess bromine. The 125-ml funnel was inverted without losing the PH_3. Nitrogen gas was introduced through the septum by a N_2-flushed syringe connected to a cylinder of N_2. The diluted PH_3 gas passed through the larger flask and the scrubber, oxidizing the PH_3 to phosphoric acid. The solutions were discarded. All operations with PH_3 and with Br_2 water were carried out in a fume hood.

PH_3 stored over dilute H_2SO_4 was slowly absorbed to an extent of about 15 ml in 10 days.

PH_3 IN TOLUENE. A 100-mg amount of each of the prepared diluted Zn_3P_2 standards in glucose, plus a fourth dilution of 0.0001% PH_3 equivalent, was placed in separate 100-ml volumetric flasks. Toluene was added to the mark and 10% H_2SO_4 added (about 7 ml) until the flasks were filled to within 1 ml of the top. The flasks were quickly stoppered and allowed to react, with occasional mixing, for 2 hr at ambient temperature. Peak heights of the PH_3 in these standards were identical with those of the same amounts of PH_3 prepared as a dilute gas in nitrogen, about 188 to 192 mm for 1 ng PH_3 at $10^4 \times 8$ attenuation.

Table II. Phosphine Recovery in Toluene from Zinc Phosphide in Sugarcane as a Function of Reaction Time

Time, hr	Phosphine recovery from zinc phosphide (%) 1.000 ppm[a]	0.100 ppm	0.010 ppm	0.001 ppm
0.5	34.1	36.4	47.2	0.0
1.0	44.4	53.8	76.1	0.0
1.5	46.1	51.3	71.8	0.0
2.0	50.5	57.1	68.0	0.0
2.5	51.5	55.9	70.4	0.0
19[b]	35.5	31.4	0.0	0.0
96[b]	10.2	0.0	0.0	0.0

[a] Phosphine equivalent on sugarcane, recovery relative to reference standards. [b] No shaking of sample or reference after 2.5 hr.

RESULTS AND DISCUSSION

The phosphorus-specific gas chromatographic procedure used to measure PH_3 in an appropriate solvent proved to be rapid and sensitive. No sample or solvent cleanup was necessary, nor was the scrupulous attention to reagent purity and glassware cleanliness required as was true of the colorimetric procedures in which PH_3 was oxidized and determined as phosphoric acid. Use of a solvent system for absorption of PH_3 proved to be more convenient than manipulation of gas samples diluted with N_2. However, the partitioning of PH_3 among the various phases reduced the amount present in the solvent and therefore reduced the recovery of PH_3 relative to an absolute standard. Also, PH_3 dissolved in a solvent was sufficiently fugitive that manipulation from closed systems was necessary if multiple injections were to be made in the gas chromatograph. Although PH_3 was readily soluble in toluene under equilibrium conditions, the gas vaporized from the solvent in the open.

The absolute sensitivity of 5 pg of PH_3 obtained by Berck *et al.* (1970) could not be duplicated, either in the gas or solvent systems, probably because of the noise level of the detector; 20 pg could easily be quantitated. No interference from other volatile phosphorus or sulfur compounds was noted from sugarcane extractives, solvent, aqueous, or gas phases of the analytical system.

Phosphine is a reactive compound; its solutions in toluene, water, or gas were not stable for prolonged periods and had

Table III. Analysis of Phosphine in Sugarcane from the Use of Zinc Phosphide Bait

Number of applications × amount of bait, lb/acre	Phosphine (ppm) found[a] at 1 week	Phosphine (ppm) found[a] at 110 days	Theoretical PH_3 in leaf axils, ppm
Honokaa Sugar Co.			
4 × 50	0.010	0.032	0.75
4 × 10	0.015	0.012	0.15
4 × 5	0.004	0.006	0.075
None	0.000	0.000	0.000
Mauna Kea Sugar Co.			
4 × 50	0.045	0.000	0.75
4 × 10	0.008	0.000	0.15
4 × 5	0.000	0.000	0.075
None	0.000	0.000	0.000

[a] Average of three replications. Rainfall from first application to each sampling date: Honokaa Sugar Co. to first sample, 29 in., total 60 in.; Mauna Kea Sugar Co. to first sample, 52 in., total 124 in.

to be freshly prepared when needed. Analyses had to be standardized as to time and temperature and compared with reference standards.

Phosphine, released by aqueous acid from zinc phosphide in a closed system, formed a partitioned equilibrium between the solid, liquid, and gaseous phases. Substantially quantitative recovery of the PH_3 was attained in toluene if the solvent occupied nearly all the volume of the containing vessel, keeping other phases to a minimum. Table I shows that the equilibrium in the present analytical system depended on volumes of solvent and gas phases rather than on the quantity of PH_3 present. The equilibrium solubility of PH_3 in water or aqueous acid was low enough (about 4% of the PH_3 present) not to require its consideration as a source of dissolved PH_3.

Sugarcane, however, did remove considerable quantities of PH_3 from the mixture after the gas had been liberated from Zn_3P_2. About 42% of the total PH_3 was absorbed by the sugarcane in the acid medium. Additional acid volume or acid strength did not release more PH_3, indicating the reaction of PH_3 with sugarcane was irreversible. These results were not unexpected. Berck (1968) and Berck and Gunther (1970) have described the irreversible absorption of PH_3 by many cereal and some mineral substrates. Further, the recoveries of PH_3 from Zn_3P_2 in sugarcane obtained with the colorimetric procedures are low. Work with $^{32}PH_3$, added to sugarcane in aqueous acid, to be reported separately, showed that about 30% of the PH_3 reacted irreversibly to form water-soluble compounds of phosphorus, while another 10% remained irreversibly bound in the fiber. The nonvolatile ^{32}P in these experiments could be totally recovered after ashing the aqueous acid medium, or sugarcane, respectively, in a furnace at 550° C. The identity of the compounds is not fully known, but it would appear that reaction occurred to phosphorus oxyacids, which would be water-soluble, and that a portion of the acid may have formed insoluble iron or aluminum salts in the fiber.

CAUTION: The release of PH_3 from Zn_3P_2 in a closed glass vessel should be confined to quantities less than a few milligrams. Larger quantities may form explosive mixtures with air or solvents, or may produce excess pressure in the sealed flasks. Although in these experiments no problem (or analytical difference) was encountered if air was left in the Erlenmeyer flasks, it is advisable to flush the flasks with N_2 just before adding acid and sealing.

Table II shows the effect of reaction time and quantity of Zn_3P_2 on the recovery of PH_3 from sugarcane. The recoveries are related to reference standards prepared in the same manner. After reaching a maximum level within a period of 2 hr, PH_3 concentrations declined, probably because of conversion of PH_3 to nonvolatile phosphorus compounds. Recoveries of PH_3 were greater from the lesser amounts of Zn_3P_2, contrary to experience with the colorimetric procedure. Phosphine at 0.001 ppm on sugarcane could not be detected.

We used the analytical method to detect the presence of PH_3 from Zn_3P_2 used as a rodenticide in sugarcane fields. Two areas, a relatively low rainfall location at Honokaa Sugar Co., and a high rainfall loaction at Mauna Kea Sugar Co., received four separate broadcast applications at 2-month intervals of the bait, 2% Zn_3P_2 (94% active) on oat groats. The normal 5 lb of bait/acre, a double quantity of 10 lb/acre and a tenfold 50 lb/acre resulted in total applications of 20, 40, and 200 lb/acre on the experimental plots. The results of two samplings, the first taken 1 week after the last application, and the second at the crop harvest 103 days later, are shown in Table III. The final samples were taken from the field prior to the normal pre-harvest burning and represent maximum residues; leaves were included. Leaf burning and removal, mechanical harvesting, and washing of stalks at the mill would all be expected to reduce residues. Our sampling procedure would give material with the maximum residues that could be present at the start of the harvesting process for that particular field.

Allowing for considerable sample variability, the sugarcane in the dry location retained part of the zinc phosphide throughout the test period, while in the wetter location it did not. These results may indicate either that Zn_3P_2 washed out of the leaf axils into the soil, or that the presence of water in the leaf axils in the wet location increased the rate or extent of decomposition of the phosphide and loss of PH_3. It is assumed that the presence of phosphine as a residue in sugarcane resulted entirely from traces of zinc phosphide remaining in the leaf axils. Assuming that 15% of the grain was originally retained by the leaf axils, the actual residues of PH_3 found in the dry location represent less than 10% of the calculated amounts that were theoretically possible from the retained Zn_3P_2.

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LITERATURE CITED

Berck, B., J. AGR. FOOD CHEM. **13,** 373 (1965).
Berck, B., J. AGR. FOOD CHEM. **16,** 419 (1968).
Berck, B., Gunther, F. A., J. AGR. FOOD CHEM. **18,** 148 (1970).
Berck, B., Westlake, W. E., Gunther, F. A., J. AGR. FOOD CHEM. **18,** 143 (1970).
Bruce, R. B., Robbins, A. J., Tuft, T. O., J. AGR. FOOD CHEM. **10,** 18 (1962).
Dumas, T., J. AGR. FOOD CHEM. **12,** 257 (1964).
Dumas, T., J. AGR. FOOD CHEM. **17,** 1164 (1969).
Hazleton Labs., Inc., in U.S. Food and Drug Administration, Pesticide Analytical Manual, Vol. II, Pesticide Reg. Sec. 120.235 Aluminum phosphide Method A, 1968.
Nass, R. D., Hood, G. A., Lindsey, G. D., *Sugar J.* **33**(1), 34 (1970).

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