Table I. Typical Recovery Data

Crop	No. of Samples	Range, P.P.B. Fortification	Recovery Range, %	Recovery Average, %
Cottonseed	33	5–100	75–110	90.7
Dried peas	6	20–80	80–105	87.5
Dried beans	16	5–100	75–110	97.9
Dried bean fodder	4	20–80	100–105	102.0
Potato	8	20–320	75–90	80.8
Melon	2	20–80	80–87.5	83.8
Cucumbers	3	20–80	90–106	98.7
Cabbage	8	20–250	70–100	91.2
Sugar beet roots	6	20–80	80–95	85.0
Sugar beet tops	6	10–80	80–100	83.3
Wax beans	15	20–80	80–105	94.2
Peanuts	2	20–40	80	80
Peanut shells	2	20–40	90–100	95
Brussels sprouts	2	20–40	100	100
Red beet tops	2	20–40	80–100	90
Red beet roots	2	20–40	80–90	85
Corn ears	2	20–40	80	80
Cornstalks	2	20–40	80–92	86.0
Tomatoes	6	20–70	85–106	98.2

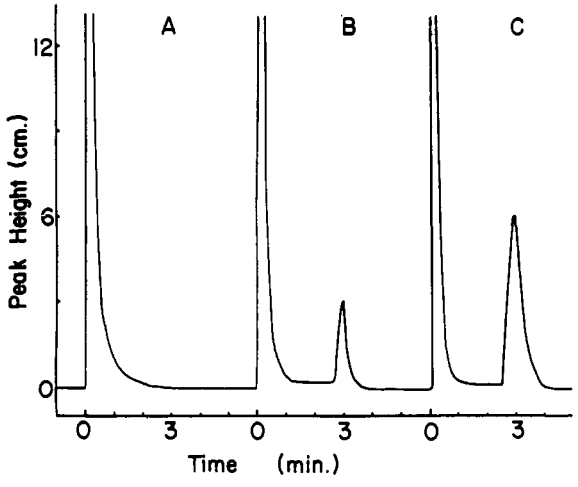

Figure 2. Typical analysis

A. Untreated red beet tops
B. Untreated red beet tops fortified with 40 p.p.b. of Lanstan
C. Standard, 200 pg. of Lanstan equivalent to 80 p.p.b.

recoveries decreased proportionately as the concentration increased.

Minor modifications to the procedure were necessary for certain crops. The highly absorptive nature of peanut shells, cornstalks, and dried bean fodder made necessary the use of twice the usual amount of benzene for extraction. Peanuts and cottonseed, because of their high oil content, were extracted with benzene or hexane. A cleanup procedure was necessary only on sugar beet tops, Brussels sprouts, and cornstalks.

Results

Although 50% of the sensitivity of the instrument was sacrificed to facilitate routine analysis, the method could easily detect 10 p.p.b. (25 pg.).

Recovery data obtained for various crops are summarized in Table I. Recoveries generally ranged between 75 and 105% after fortifications of 10 to 100 p.p.b. were made.

A typical analysis is illustrated in Figure 2. The complete absence of interference from the crop can be observed, although no cleanup procedure is used.

All crops were treated with 1 to 4 pounds of Lanstan per acre at time of planting and were sampled at harvest time.

No residues greater than the sensitivity of the method were detected. The speed of analysis was excellent. A sample could usually be injected into the instrument every 5 minutes.

Literature Cited

(1) Beckman, H., Bevenue, A., J. Agr. Food Chem. **6**, 479–82 (1963).

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HERBICIDE RESIDUES

Use of Microcoulometric Gas Chromatograph for Triazine Herbicides

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A variety of *s*-triazine herbicides are used for weed control in crops. Therefore, specific methods for residue determination are needed. Some of the published methods for determining microgram quantities of triazines have general application to triazines, whereas others are applicable to certain triazines only. A colorimetric method applicable to the chlorotriazines only involves the Zincke reaction (*5*, *6*).

In this laboratory, an ultraviolet method is used (*3*), which is applicable to all the commonly used *s*-triazine herbicides. Final determinations are made by converting the *s*-triazines to their hydroxy derivative and measuring the absorbance in the ultraviolet region. Neither the colorimetric nor ultraviolet method distinguishes between the various triazine herbicides.

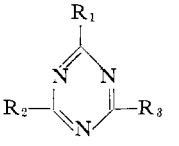
Gas chromatography offers a specific method for determining individual members of the triazine herbicides. Gas chromatography has been used for residue analyses (*1*), with a Pye argon chromatograph.

A series of technical triazines was investigated by Stammbach and coworkers (*7*) using gas chromatography and both thermal conductivity and flame ionization detectors. Henkel and Ebing (*4*) have used gas chromatography

The Dohrmann microcoulometric gas chromatograph has been applied to the determination of various chloro- and thiomethyltriazine residues in crop materials. Of the columns evaluated, Carbowax 20M resolves the triazines best. A cleanup method applicable to a number of crops has been developed. Excellent recoveries were obtained from known amounts of triazine herbicides added to crop materials before extraction. Results agreed well with those obtained by the conventional ultraviolet method.

for determining triazines in soils fortified at 0.5 to 3.0 p.p.m., using flame ionization detection. The Dohrmann microcoulometric gas chromatograph has been developed for the determination of pesticide residues (*2*). We applied this instrument to the determination of *s*-triazine residues (Table I).

Table I. Structure of Triazines Investigated



Common Name	R_1	R_2	R_3	% S	% Cl
Atrazine	Cl	NHC_2H_5	$NHCH(CH_3)_2$	...	16.44
Propazine	Cl	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	...	15.46
Simazine	Cl	NHC_2H_5	NHC_2H_5	...	17.58
Ametryne	SCH_3	NHC_2H_5	$NHCH(CH_3)_2$	14.13	...
Prometryne	SCH_3	$NHCH(CH_3)_2$	$NHCH(CH_3)_2$	13.30	...
Simetryne	SCH_3	NHC_2H_5	NHC_2H_5	15.05	...

Table II. Elution Times and Retention Relative to Propazine and Prometryne of Some s-Triazine Herbicides

Compound	GC Column Substrate	%	Temp., ° C. Column	Temp., ° C. Injection Block	Column Nitrogen Flow, Cm.	Elution Time, Min.	Relative Retention
Propazine	Carbowax 20M	5	215	225	3.0	4.8	1.00
Atrazine	Carbowax 20M	5	215	225	3.0	6.2	1.29
Simazine	Carbowax 20M	5	215	225	3.0	7.8	1.63
Prometryne	Carbowax 20M	5	215	225	2.0	6.2	1.00
Ametryne	Carbowax 20M	5	215	225	2.0	7.8	1.26
Simetryne	Carbowax 20M	5	215	225	2.0	9.8	1.58
Prometryne	Carbowax 20M	10	240	250	4.5	7.0	1.00
Ametryne	Carbowax 20M	10	240	250	4.5	8.8	1.26
Simetryne	Carbowax 20M	10	240	250	4.5	10.9	1.56
Propazine	GE nitrile silicone	5	190	200	3.5	6.8	1.00
Atrazine	GE nitrile silicone	5	190	200	3.5	7.9	1.16
Simazine	GE nitrile silicone	5	190	200	3.5	8.6	1.26
Propazine	Apiezon L	5	185	210	4.0	4.0	1.00
Atrazine	Apiezon L	5	185	210	4.0	4.0	1.00
Simazine	Apiezon L	5	185	210	4.0	4.0	1.00

Extraction and Cleanup of Crop Samples

The crops are chopped in a Hobart food cutter. Two hundred grams of the chopped sample are mixed with 500 ml. of chloroform in a 1-quart jar and shaken for one-half hour on a mechanical shaker. The extract is filtered through filter paper and dried with anhydrous sodium sulfate. An aliquot equivalent to 10 to 20 grams is evaporated to dryness using a flash evaporator. The residue is taken up in 2 ml. of benzene.

Aluminum oxide of Activity V (Woelm) is used for cleanup. Twelve grams of aluminum oxide, Activity V, are packed into a chromatographic column (20 mm. I.D. × 180 mm.). The benzene solution is then transferred to the column, and the sample is washed into the column with small amounts of *n*-hexane. The column is eluted with a total of 75 ml. of *n*-hexane. No triazines are eluted by this eluate. They are quantitatively recovered from the column with 150 ml. of a mixture of 1 to 1 benzene-hexane. This solution is evaporated to dryness using a flash evaporator. The residue is transferred quantitatively to a 10-ml. centrifuge tube with ethyl ether. The ethyl ether is evaporated to dryness, and the residue is dissolved in a small known volume of benzene (usually 0.5 ml.). Aliquots of this solution are used for gas chromatography.

Gas Chromatographic Procedure

A Dohrmann microcoulometric gas chromatograph equipped with a T-200-s titration cell sensitive to halides and a T-200-s titration cell sensitive to sulfur was used in this work. The injection port was fitted with a replaceable Vycor insert, in which platinum gauze and quartz wool were used. Columns, 5 feet long, were made from 1/4-inch aluminum tubing. Carbowax 20M, GE Nitrile Silicon Gum XE 60, and Apiezon L on Anakrom ABS were used as stationary phases at various concentrations. Various temperature conditions were utilized. The flow rates ranged from a gage reading of 2 cm. (approximately 50 ml. per minute) to 4.0 cm. (approximately 100 ml. per minute). Volumes of 10 to 100 μl. of solution were injected. The range setting was 128 ohms throughout this work. The columns were conditioned with the triazines to be determined until constant recoveries were obtained. The areas of the peaks obtained from standard material were calculated in terms of square inches per microgram of triazine injected. The triazine found for unknown samples was calculated using this figure.

Ultraviolet Procedure

This procedure depends on converting the chloro- and thiomethyltriazines to the hydroxy compound. The hydroxytriazines have an absorption maximum at 240 mμ. This method does not differentiate between the triazines but gives the total amount of these compounds present. In the present study, the crop samples analyzed were of known history and were known to have been treated with a particular triazine. This method has been used extensively for a number of triazines and a wide variety of crops. It has given excellent recovery of known amounts of triazines.

Results and Discussion

Typical data are shown in Table II for different columns and conditions for the chromatography of standard materials. The relative retention time is calculated for each set of conditions and related to Propazine for the chlorotriazines and to Prometryne for the thiomethyltriazines.

All columns used allow the triazines to be chromatographed. The column showing the best resolution was the Carbowax 20M, which in combination with the specificity of the titration cells allows qualitative and quantitative identification of the six triazines studied. The GE Nitrile Silicone XE 60 column

Table III. Recovery of Triazines from Crop Samples Fortified before Extraction

Triazines	Crop	Equivalent Sample Weight Injected, Grams	Triazine Added P.p.m.	Triazine Added µg.	Triazine Recovered P.p.m.	Triazine Recovered µg.	Triazine Recovered %	Chromatographic Column Used
Atrazine	Soybean	4.0	0.05	0.20	0.05	0.18	90	GE nitrile silicone (5%)
			0.10	0.40	0.09	0.36	90	GE nitrile silicone (5%)
	Wheat straw	2.5	0.10	0.25	0.08	0.21	84	GE nitrile silicone (5%)
			0.10	0.25	0.08	0.21	84	GE nitrile silicone (5%)
Ametryne	Sugar cane	3.0	0.10	0.30	0.11	0.32	107	Carbowax 20M (5%)
			0.05	0.15	0.05	0.16	107	Carbowax 20M (5%)
	Potato tubers	2.0	0.20	0.40	0.18	0.36	90	Carbowax 20M (5%)
	Pineapple foliage	6.3	0.04	0.23	0.03	0.19	75	Carbowax 20M (5%)
Prometryne	Peanut foliage	2.0	0.20	0.40	0.21	0.42	105	GE nitrile silicone (5%)

Table IV. s-Triazine Residues in Crop Materials Determined by Gas Chromatography and Ultraviolet Method

Triazine Found	Crop	Triazine Found, P.P.M. MCGC	Triazine Found, P.P.M. Ultraviolet	GC Column
Atrazine	Pineapple foliage	1.5	1.7	GE nitrile silicone
		1.8	1.7	GE nitrile silicone
		1.8	1.8	GE nitrile silicone
		2.8	2.8	GE nitrile silicone
		13	12	Carbowax 20M
		26	32	Carbowax 20M
		34	38	Carbowax 20M
	Wheat grain	0.14	0.27	GE nitrile silicone
		0.26	0.30	GE nitrile silicone
		0.50	0.43	GE nitrile silicone
	Wheat straw	0.08	0.10	GE nitrile silicone
		0.40	0.50	GE nitrile silicone
		0.18	0.17	GE nitrile silicone
	Soybean foliage	0.06	0.08	GE nitrile silicone
		0.05	0.06	GE nitrile silicone
Prometryne	Peanut foliage	0.13	0.13	GE nitrile silicone
		0.23	0.19	GE nitrile silicone
Ametryne	Sugar cane	0.08	0.09	Carbowax 20M
		0.16	0.19	Carbowax 20M
		0.67	0.68	Carbowax 20M
		0.79	0.72	Carbowax 20M
		0.74	0.75	Carbowax 20M
		2.3	2.0	Carbowax 20M

also separates the triazines, but not as well as the Carbowax 20M. However, slightly lower temperatures can be used with this column. The triazines can be chromatographed on an Apiezon L column but no resolution of the various triazines was evident.

Recoveries of standards show considerable variation, depending on column conditioning, type of samples analyzed, and unknown factors. The amount of extraneous material in a series of samples can have a large influence in reducing recoveries of standards injected subsequently. The wide range of recoveries of standard materials seems to be inherent in the use of vapor phase chromatography for the determination of residues at low levels. To obtain reliable results, standards must be run frequently.

Table III shows recoveries of triazines added to crop samples before extraction but after the complete cleanup procedure. Sensitivity of the GC method for the triazine herbicides depends appreciably on the kind of crop sample being analyzed and how well extraneous materials can be removed. For most crop samples, 0.25 µg. of triazine can be measured quantitatively in the presence of the equivalent of 5 grams of crop extract (0.05 p.p.m.). Less than 0.05 p.p.m. can be determined with crop extracts containing low amounts of impurities. With the more difficult samples, values much lower than 0.05 p.p.m. can be obtained only at the expense of considerable time and effort in cleanup of the injection block and conditioning of the column. This sharply reduces the number of samples that can be run. A sensitivity setting of 128 ohms was generally used. With the instrument used for this work, this setting was found to be the most sensitive position that gave satisfactory results. Use of the increased sensitivity setting, 256 and 512 ohms, increased the noise level so much that no advantage was gained.

Comparison of Methods

Table IV shows gas chromatographic results compared with those obtained by the conventional ultraviolet method. The excellent correlation between the two methods establishes confidence in both methods.

Literature Cited

(1) Chilwell, E. D., Hughes, D., *J. Sci. Food Agr.* **13,** 425–7 (1962).
(2) Coulson, D. M., Cavanagh, L. A., DeVries, J. D., Walther, B., J. AGR. FOOD CHEM. **8,** 399 (1959).
(3) Gysin, H., Knüsli, E., *Advan. Pest Control Res.* **3,** 289–358 (1960).
(4) Henkel, H. G., Ebing, W., *J. Gas Chromatog.* **2,** 215–18 (1964).
(5) Ragab, M. T. A., Ph.D. thesis, University of Illinois, Urbana, 1959.
(6) Ragab, M. T. A., McCallum, T. P., "Colorimetric Methods for the Determination of Simazine and Related Chloro-*s*-triazines," Division of Agricultural and Food Chemistry, 147th Meeting, ACS, Philadelphia, Pa., 1964.
(7) Stammbach, K., Kilcher, H., Friederich, K., Larsen, M., Székely, G., *Weed Res.* **4,** 64–74 (1964).

Received for review August 21, 1964. Accepted December 11, 1964.