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QUANTITATIVE ANALYSIS OF *s*-TRIAZINE HERBICIDES BY GLASS CAPILLARY COLUMN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The quantitative analysis of *s*-triazines in model mixtures and real samples was performed on a glass capillary column, which is convenient for multi-component analyses, with Carbowax 20M as stationary, with two detection systems, *viz.*, a flame-ionization detector (FID) and an alkali flame detector (AFD). The range of linear response of both the FID (the range range studied was 10–2000 ng of six *s*-triazines) and the AFD (the range studied was 1–200 ng of four *s*-triazines) was determined. Analytical curves were evaluated by linear regression. The limit of detection (amount which gives a peak equivalent to three times the baseline noise) of injected standards was found to be 5–10 ng of *s*-triazines with an inlet splitting ratio of 1:90 for the FID and 50–70 pg for the AFD at an inlet splitting ratio of 1:20.

By comparing the results of quantitative analyses on glass capillary columns and packed columns it was determined that the same results could be obtained on both, but on the former it is possible to analyse quantitatively multi-component residues of *s*-triazines in envitonmental samples.

INTRODUCTION

s-Triazines are among the most widely used herbicides, and contaminate the environment with undesirable residues. Numerous analytical procedures are available for determining residues of *s*-triazines in different materials such as soils, waters and plant materials.

Colorimetric[1,2] and UV spectrophotometric methods[3,4] have been used for the determination of *s*-triazines. These methods, however, allow the determination of only one individual triazine in one analysis and can be applied to the analysis of samples of unknown history only with difficulty.

For several years chromatographic procedures[5,6], paper chromatography, thin-layer chromatography gas–liquid chromatography (GLC), and recently even high-performance liquid chromatography[7–9] and high-performance thin-layer chromatography[9] have been applied for the separation, identification and determination of these substances and their metabolic and degradation products from environmental

residue sources and from tissues. GLC with packed columns has played a major role in the analysis of *s*-triazine residues. Various detectors, such as the flame-ionization detector (FID)[10–12], electron-capture detector[13–15], microcoulometric detector[13,16], alkali flame detector (AFD)[17–21], flame photometric detector[22] and electrolytic conductivity detector[14,15,20,21,23–27], have been used.

We have previously introduced[28,29] high-resolution glass capillary columns in the analysis of *s*-triazines. A multi-component mixture of chloro-, methoxy- and methylthio-*s*-triazines was separated successfully on Carbowax 20M glass capillary columns.

The aim of this work was to evaluate the possibilities of glass capillary column GLC with an FID or alkali flame detector in the quantitative analysis of *s*-triazines, mainly at residue concentration levels, and to compare these results with those obtained on packed columns.

EXPERIMENTAL

Apparatus

A Carlo Erba Model 2350 gas chromatograph equipped with an FID and a thermionic nitrogen–phosphorus-specific detector (NPSD) with a potassium chloride pellet in the nitrogen mode was used, and with glass capillaries a stream splitter was employed. The narrow ends of the glass capillary columns were led directly to the splitter or to the jet of the detector with the FID and or to just under the jet of the detector with the NPSD, as the introduction of make-up gas was necessary.

The thermostat was maintained at 473°K and the injection block temperature was 548°K. An Autolab Model 6300 digital integrator and a calibrated magnifying glass were used for peak-area measurements.

A glass column packed with 3% Carbowax 20M on 80–100-mesh Chromosorb W AW (1.3 m × 3.3 mm I.D.) was used. The carrier gas was nitrogen at a flow-rate of 47 ml/min, the hydrogen flow-rate was 35 ml/min and the air flow-rate 255 ml/min.

Glass capillary columns made of soft soda-lime glass[28] dynamically coated with 10% Carbowax 20M (27.0 and 11.0 m × 0.24 mm I.D.) were used. The conditions with the FID were as follows: carrier gas, nitrogen at a flow-rate of 1.1 ml/min; hydrogen flow-rate, 22.0 ml/min; air flow-rate, 361.0 ml/min. The conditions with the NPSD in the nitrogen mode were as follows: carrier gas, nitrogen at a flow-rate with make-up gas of 40.0 ml/min; hydrogen flow-rate, 30.0 ml/min; air flow-rate, 286.0 ml/min.

Chemicals

The common and systematic names of used *s*-triazines are given in Table I. All were standard materials from Ciba-Geigy (Basle, Switzerland).

The solvents used were of analytical-reagent grade and were distilled prior to use.

Preparation of standard solutions

Standard solutions of *s*-triazines were prepared by dissolving 0.5–10.0 mg of the solid in 10 ml of chloroform with the FID or in 10 ml of ethyl acetate with the NSPD. Solutions of lower concentrations were prepared by dilution.

TABLE I

s-TRIAZINES STUDIED

Detector used	*Common name*	*Systematic name*
FID	Terbuton	2-Methoxy-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
	Propazine	2-Chloro-4,6-bis(isopropylamino)-*s*-triazine
	Terbutylazine	2-Chloro-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
	Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
	Terbutryn	2-Methylthio-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
	Simazine	2-Chloro-4,6-bis(ethylamino)-*s*-triazine
AFD	Propazine	2-Chloro-4,6-bis(isopropylamino)-*s*-triazine
	Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
	Prometryn	2-Methylthio-4,6-bis(isopropylamino)-*s*-triazine
	Simazine	2-Chloro-4,6-bis(ethylamino)-*s*-triazine

RESULTS AND DISCUSSION

As the best results in the separation of complex *s*-triazine mixtures on glass capillary columns have previously been achieved with Carbowax 20M as the stationary phase, the quantitative analysis of the chosen *s*-triazines was performed on this stationary phase.

We studied the range of linear response of the detector, the limit of detection

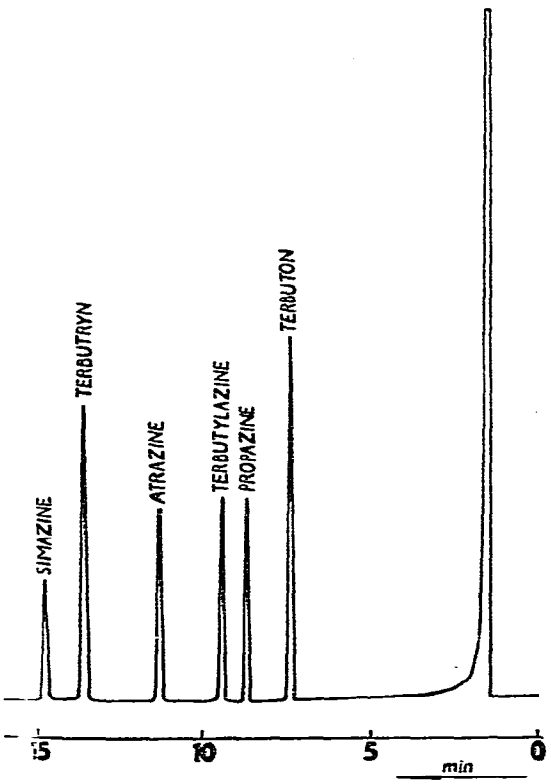


Fig. 1. Separation of a model mixture of six *s*-triazines on a Carbowax 20M glass capillary column (7.0 m long) used for quantitative analysis with an FID at an inlet splitting ratio of 1:90.

and the reproducibility of measurements using the FID and the AFD. The results obtained on capillary columns were compared with those obtained on packed columns.

Flame-ionization detector

In glass capillary column GLC (inlet splitting ratio 1:90), for the determination of the range of linear response of the FID a model mixture of six *s*-triazines was used. Their separation is shown in Fig. 1. It was found that the response of the detector was linear in the range 10–2000 ng of injected *s*-triazines. For peak-area measurements the methods of peak height × width at half-height (determined with a calibrated magnifying glass with a read-out precision ± 0.05 mm) and digital integration were used. Calibration graph was constructed by plotting the peak area against the amount of *s*-triazines injected. The sample was injected by the washed-out plug of solvent technique. The results of the calibration graphs ($n \geqslant 15$) were statistically evaluated by linear regression. It was found that the sample injection volume was a very critical factor when the inlet splitting system was used. On the injection of different volumes (0.5–3.0 μl) of standard solutions, in spite of the fact that the calibration graph was linear (with magnifying glass measurements of the peak area the correlation coefficient for *s*-triazines was 0.982–0.988 and with digital integration 0.993–0.994), the straight lines did not pass through the origin, from which follows the systematic error of the

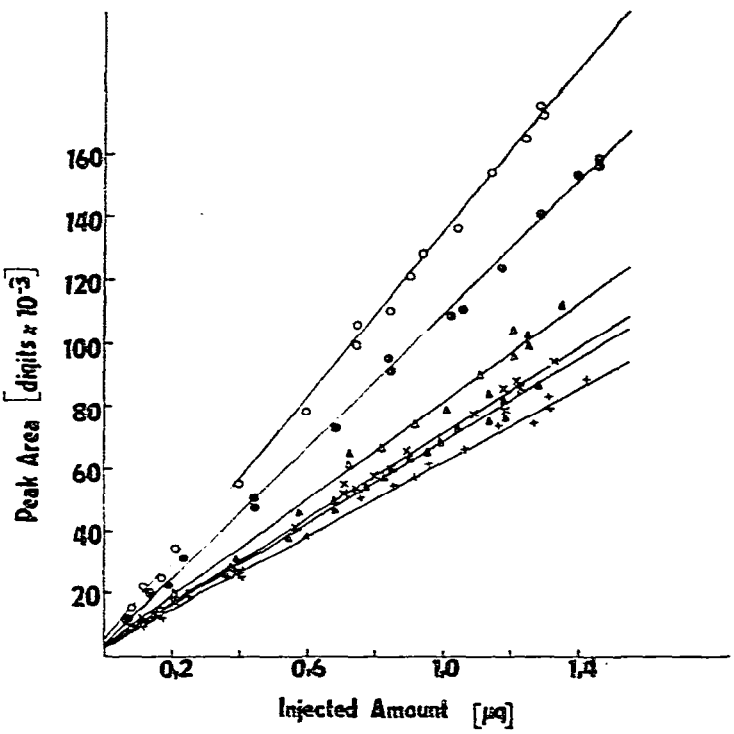


Fig. 2. Calibration graphs for *s*-triazines analysed on a Carbowax 20M glass capillary column with an FID in the concentration range 0.05–1.40 μg using different injection volumes and an inlet splitting ratio of 1:90. Peak area digits given by integrator. +, Simazine; ▲, propazine; ×, terbutylazine; △, atrazine; ●, terbutin; ○, terbutryn.

analysis. The average value of the intercept on the *y*-axis was over 2% of the maximal value (Fig. 2).

On the injection of equal volumes (1.5 μl) of *s*-triazine standard solutions of different concentrations (standard solutions were prepared by dilution), the straight lines obtained passed through the origin, the average value of the intercept on the *y*-axis being negligible (0.00014% of the maximal *y* value) and the correlation coefficient was 0.995–0.996.

As the reproducibility of measurements is very important in quantitative analysis, we investigated the reproducibility of an injection. After statistically evaluating *s*-triazine peak areas for an individual injection (1.5 μl of a standard solution of *s*-triazines) for $n = 7$, the mean value of the standard deviation (S_m) of individual standards was 3.14% (at the 95% confidence level).

The limit of detection (three times the baseline noise) of six injected standards of *s*-triazines with an inlet splitting ratio of 1:90 was found to be 5–10 ng.

Real samples with low concentrations of *s*-triazines could be also analysed with the FID when a lower inlet splitting ratio was used. The limit of detection of

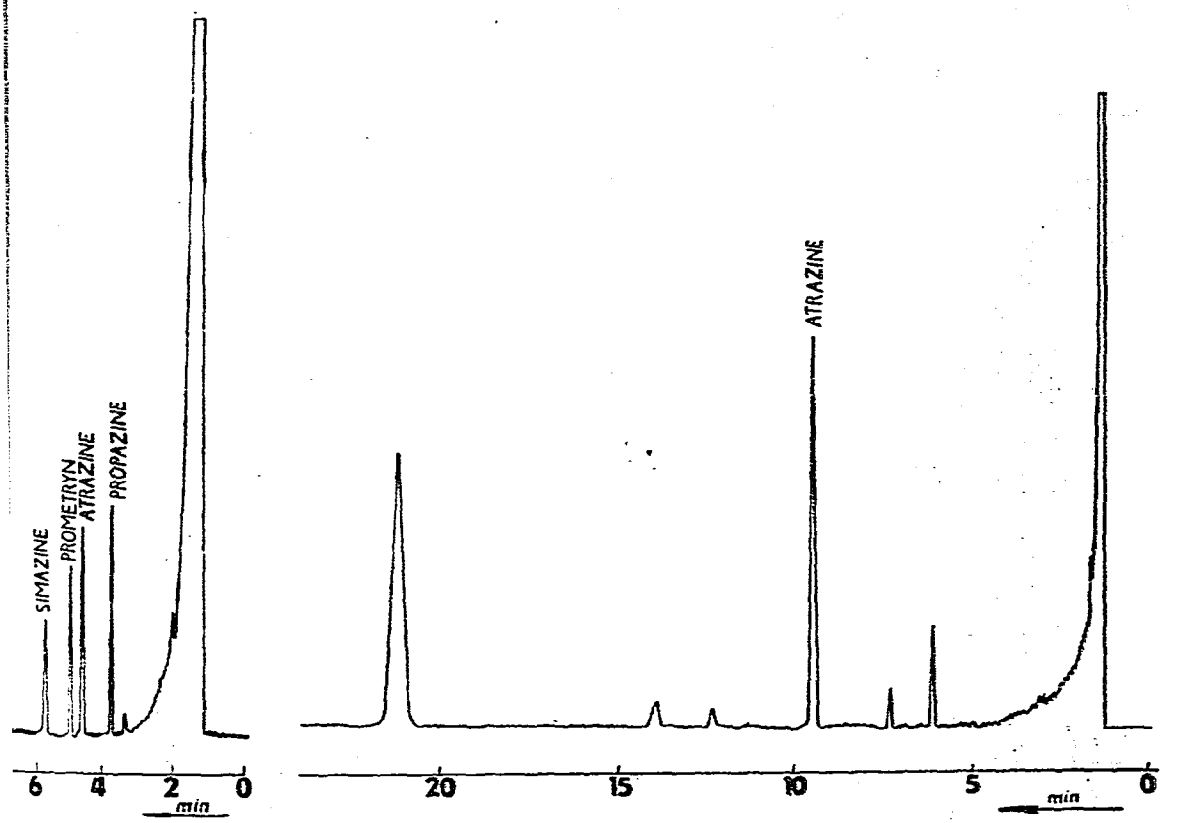


Fig. 3. Gas chromatogram of water extract of *s*-triazines (50 μg/kg) with an inlet splitting ratio of 1:15 using an FID. One litre of water was taken for extraction; 1.5 μl was injected from the final volume of 5 ml.

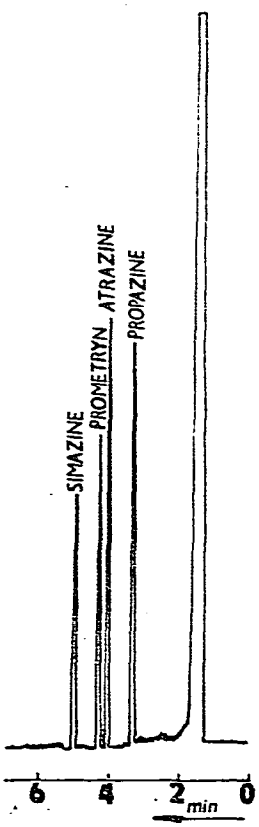
Fig. 4. Gas chromatogram of soil extract of atrazine (5 mg/kg) with an inlet splitting ratio of 1:15 using an FID. Fifty grams of soil sample were taken for extraction; 1.5 μl was injected from the final volume of 5 ml.

atrazine with an inlet splitting ratio of 1:15 was found to be 0.5 ng. The analyses of real samples of *s*-triazines in a water extract and a soil extract are shown in Figs. 3 and 4. The extractions were performed at the Water Management Research Institute in Bratislava[30].

For a comparison of the quantitative results measured on Carbowax 20M glass capillary columns, the quantitative analysis was also performed on a column packed with Carbowax 20M.

The linear response of the FID on the Carbowax 20M packed column was checked for the range 50–4000 ng of injected atrazine. The reproducibility of the injection expressed as the standard deviation (S_m) of the peak area for $n = 7$ was 1.49% (at the 95% confidence level).

After the evaluation of the calibration graph by linear regression, the correlation coefficient was 0.998–0.999. The limit of detection of atrazine was 6 ng, which is comparable to the value determined on a glass capillary column with an inlet splitting ratio of 1:90.



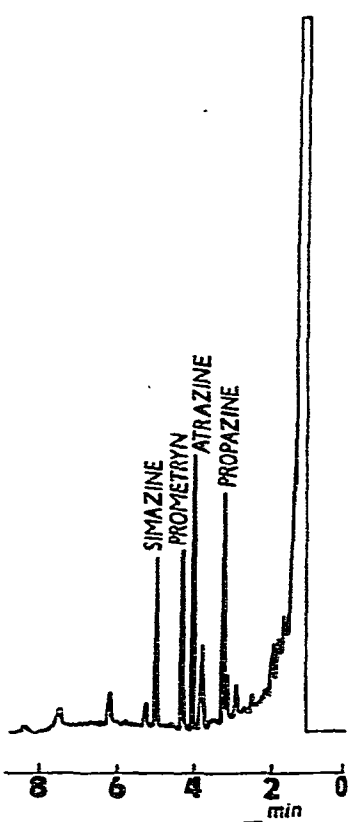


Fig. 5. Separation of four *s*-triazines used as a model mixture for quantitative analysis on a Carbowax 20M glass capillary column (11.0 m long) with an AFD and an inlet splitting ratio of 1:20.

Fig. 6. Gas chromatogram of water extract of *s*-triazines (0.1 μg/kg) using an AFD. One litre of water was extracted to give a final volume of 0.2 ml; 1.5 μl was injected at with an inlet splitting ratio of 1:20.

Alkali flame detector

For the analysis of *s*-triazines in by capillary column GLC an AFD was used, which previously had been used only with packed columns. To operate the detector under optimal conditions, a make-up gas (nitrogen) was used.

The separation of four *s*-triazines, which were used as a model mixture for quantitative analysis with the AFD on a Carbowax 20M glass capillary column is shown in Fig. 5. The response of the detector was linear for injected amounts of 1–200 ng of *s*-triazines. After statistical evaluation of the calibration graphs ($n \geqslant 15$) by linear regression the correlation coefficient was 0.929–0.996. The reproducibility of measurement was determined by repeated injections of the same volume (1.5 μl) of a standard solution of *s*-triazines. After statistically evaluating the peak area at individual injections ($n = 7$), the mean value of the standard deviation (S_m) for individual standards was 4.59% (at the 95% confidence level).

The limit of the detection (three times the baseline noise) with four injected standards of *s*-triazines with an inlet splitting ratio of 1:20 was found to be 50–70 pg. The analysis of a real sample of *s*-triazines in a water extract is shown in Fig. 6.

For a comparison, we also present the results of the quantitative analysis of atrazine on a Carbowax 20M packed column. The reproducibility of an injection expressed as the standard deviation (S_m) of the peak area for $n = 7$ was 1.52% (at the 95% confidence level). The reproducibility of measurement in this instance was higher than that with a capillary column. The correlation coefficient of the calibration graph was 0.998–0.999. The limit of detection of atrazine was 60 pg, which is comparable to the value determined on a glass capillary column. The limit of detection on a packed column represents a 100-fold higher sensitivity than with the FID and is in agreement with Verga and Poy's[31] results on the sensitivity of this detector for nitrogen-containing substances.

Comparing the results of quantitative analyses on capillary and packed columns with either an FID or an AFD, it is evident that the same results could be obtained with both .However the advantage of capillary columns is the possibility of analysing multi-component residues of *s*-triazines in environmental samples.

REFERENCES

1 H. P. Burchfield and E. E. Storrs, *Contrib. Boyce Thompson Inst.*, 18 (1956) 319.
2 H. P. Burchfield and P. H. Schuldt, *J. Agr. Food Chem.*, 6 (1958) 105.
3 H. Gysin and E. Knüsli, *Advan. Pest Contr. Res.*, 3 (1960) 289.
4 E. Knüsli, H. P. Burchfield and E. E. Storrs, *Anal. Methods Pestic. Plant Growth Regul. Food Additives*, 4 (1964) 213.
5 L. Fishbein, *Chromatogr. Rev.*, 12 (1970) 167.
6 W. P. Cochrane and R. Purkayastha, *Toxicol. Envir. Chem. Rev.*, 1 (1973) 137.
7 T. H. Byast and E. G. Cotterill, *J. Chromatogr.*, 104 (1975) 211.
8 T. Vitali, E. Gaetani, C. F. Laureri and C. Branca, *Farmaco., Ed. Sci.*, 31 (1976) 58.
9 H. Jork and B. Roth, *J. Chromatogr.*, 144 (1977) 39.
10 E. D. Chilwell and D. Hughes, *J. Sci. Food Agr.*, 13 (1962) 425.
11 H. G. Henkel and W. Ebing, *J. Chromatogr.*, 19 (1964) 283.
12 C. A. Benfield and E. D. Chilwell, *Analyst (London)*, 89 (1964) 475.
13 J. A. Burke and W. Holswade, *J. Ass. Offic. Anal. Chem.*, 49 (1966) 374.
14 W. P. Cochrane and B. P. Wilson, *J. Chromatogr.*, 63 (1971) 364.
15 R. Purkayastha and W. P. Cochrane, *J. Agr. Food Chem.*, 21 (1973) 93.
16 A. M. Mattson, R. A. Kahrs and J. Schneller, *J. Agr. Food Chem.*, 13 (1965) 120.

17 R. C. Tindle, C. W. Gehrke and W. A. Aue, *J. Ass. Offic. Anal. Chem.*, 51 (1968) 682.
18 W. Ebing, *Chromatographia*, 1 (1968) 382.
19 D. R. Schultz, *Bull. Environ. Contam. Toxicol.*, 5 (1970) 6.
20 R. Greenhalgh and W. P. Cochrane, *J. Chromatogr.*, 70 (1972) 37.
21 S. U. Khan and R. Purkayastha, *J. Agr. Food Chem.*, 23 (1975) 311.
22 A. M. Mattson, R. A. Kahrs and R. T. Murphy, *Residue Rev.*, 32 (1970) 371.
23 W. E. Westlake, A. Westlake and F. A. Gunther, *J. Agr. Food Chem.*, 18 (1970) 685.
24 W. P. Cochrane, B. P. Wilson and R. Greenhalgh, *J. Chromatogr.*, 75 (1973) 207.
25 B. P. Wilson and W. P. Cochrane, *J. Chromatogr.*, 106 (1975) 174.
26 J. F. Lawrence, *J. Chromatogr.*, 121 (1976) 85.
27 J. F. Lawrence, *J. Chromatogr.*, 128 (1976) 154.
28 E. Matisová and J. Krupčík, *J. Chromatogr.*, 142 (1977) 597.
29 E. Matisová, J. Krupčík, O. Liška and N. Szentiványi, *J. Chromatogr.*, 169 (1979) 261.
30 J. Hesler and B. Arochová, unpublished results.
31 G. R. Verga and F. Poy, *J. Chromatogr.*, 116 (1976) 17.