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Note

Gas–liquid chromatographic determination of pyridazinones in waste waters. I.

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Pyridazinones are currently used because of their biological properties as active ingredients in pharmaceutical preparations[1] and as pre- and post-emergent herbicides[2,3]. 5-Amino-4-chloro-2-phenyl-3(2*H*)-pyridazinone (PCA, common name pyrazon) is the active ingredient of herbicide formulations known under the trade names Burex, Chlorazine, Pyramin and Phenazon, which are used for weed control, particularly for sugar beet and beet crops. The main impurities in the technical products and formulations are 4-amino-5-chloro-2-phenyl-3(2*H*)-pyridazinone (i-PCA), the non-active pyrazon isomer, and 4,5-dichloro-2-phenyl-3(2*H*)-pyridazinone, the unreacted derivative (PCC), which is significant from the point of view of toxicology.

Several methods of analysis for the substances in technical products have been reported in literature: potentiometry[4], polarography[5] and spectrometry[6]. However, none selectively determines all components of the above mixture. A thin-layer chromatographic (TLC) method[7] was used to separate every component for subsequent quantitation by UV spectrophotometry, but results have not proved satisfactory because of the photolability of pyridazinones adsorbed on silica gel[8]. A gas–liquid chromatographic (GLC) method was also introduced[9]. Simultaneous determination[10] of the active ingredient and of by-products in technical and formulated pyridazinones was rapidly performed. A semi-quantitative method[11] has been proposed for the determination of PCA in water, which involves extraction with chloroform–ethyl acetate, separation by TLC and a visual estimation of the level of pyrazon by comparison with reference plates. We have developed a specific analytical method for determination of the active ingradient in the waste water used in the technological processes in the presence of many impurities.

EXPERIMENTAL

Chemicals

The pyridazinones listed in Table I were analytical grade standard materials obtained from Research Institute of Agrochemical Technology, Bratislava, Czechoslovakia.

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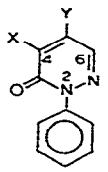
TABLE I

PYRIDAZINONES



Substance	*Substituents*	
	X	*Y*
PCA	Cl	NH_2
i-PCA	NH_2	Cl
PCC	Cl	Cl

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

Apparatus

A Carlo Erba Model 2350 gas chromatograph equipped with a flame-ionization detector (FID) was used. The thermostat was maintained at 473°K and 493°K, respectively; an injection block temperature of 498°K was used.

A glass column (0.6 m × 3.5 mm I.D.) packed with 2% OV-17 (Chrompack, The Netherlands) on 60–70 mesh Chromaton N AW DMCS (Lachema, Brno, Czechoslovakia) was employed. The carrier gas was nitrogen at a pressure of 20.3 kPa and 25.3 kPa, respectively.

A 350 rotary evaporator (Unipan, Warsaw, Poland) was used.

Procedure

Extraction was performed in a round-bottomed flask using a shaking machine.

Water samples, 100 or 500 ml, were extracted three times for 15 min with 25- and 100-ml portions of chloroform, respectively. Chloroform extracts were separated in a separating funnel. The extracts were combined and evaporated to dryness using a rotary evaporator. The residues were dissolved in a suitable defined volume of chloroform. A 1–5-μl volume of the solution was injected into the column with a 10-μl Hamilton syringe.

The recovery determination was performed in the same way using model samples of PCA and PCC of 1 mg/l concentration in distilled water.

Calibration graphs

Calibration graphs were prepared from standard solutions containing 0.5–10.0 mg of solid substance in 10 ml of chloroform. Solutions of lower concentration were prepared by dilution.

RESULTS AND DISCUSSION

Since PCA, i-PCA and PCC differ in polarity, the choice of the stationary

TABLE II

RECOVERY OF PCA AND PCC EXTRACTION, AVERAGE RECOVERY AND STANDARD DEVIATION

Substance	*Recovery (%)*	*Average recovery (%)*	*Standard deviation*
PCA	91.27 90.56 95.83	92.55	3.10
PCC	96.90 96.16 100.60	97.89	2.62

phase is significant for the efficiency of analysis. Cellerino and Re[10] tested several stationary phases. For substances of high boiling point they considered polyglycols and polyesters to be unsuitable, and silicones of lower polarity (SE-30, OV-1, OV-101, OV-7) gave unsymmetrical peaks. The OV-17 column had excellent reproducibility and column life, but the shape of PCA peak was not quite symmetrical. As the peak symmetry at the residue level is very important, we tried to prepare a column that would give perfect symmetry of all peaks. The first essential was an inert support material. Higher stationary phase loading, which diminishes the influence of support material active sites, resulted in long analysis times.

We tested several columns and achieved excellent results with a Carbowax 20M column and non-polar stationary phases of the silicone type with Carbowax 20M deactivated support material[12] in the analysis of standard solutions of PCA, i-PCA and PCC in chloroform. However, after repeated injection of water extracts of these substances very unsymmetrical peaks of PCA were observed. Unlike i-PCA, which preferentially forms intramolecular hydrogen bonds owing to the acidic hydrogen atom in the amino group, PCA forms intermolecular hydrogen bonds, which is the reason for the peak tailing.

Thus all further determinations of the above-mentioned substances in water extracts were performed on a Chromaton N AW DMCS column with 2% OV-17.

Recovery values of extraction were determined by adding known amounts of the individual pyridazinones to untreated samples (distilled water) before the extraction procedure. The average recoveries of three different samples and standard deviations were calculated and are given in Table II. These values are acceptable for residue analysis.

In the quantitative analysis we studied the linear response range of the FID, limit of detection and the reproducibility of measurements. It was found that in the studied range of 0.05–5.00 μg of injected PCA and 0.01–2.00 μg of PCC the response of the detector was linear. For peak area measurement, the methods of height multiplied by width at half height (determined by a calibrated magnifying glass with readout precision $\pm$0.05 mm) was used. An analytical curve was constructed from values of the peak area and height, respectively, and the dependence on the injected amount of pyridazinones. The sample was injected by the washed-out plug of solvent technique. The results of the analytical curves ($n \geq 15$) were statistically evaluated by linear regression. We have tested the calculated value b of straight lines $y = ax + b$,

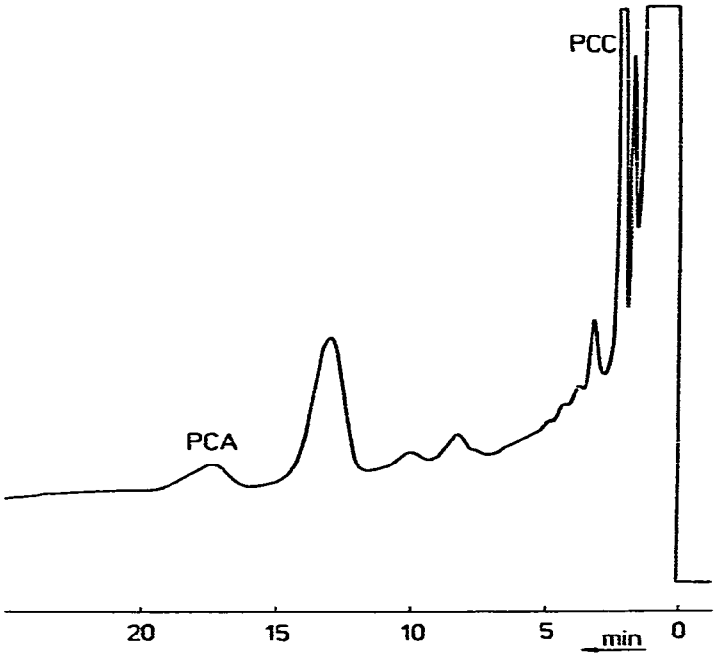


Fig. 1. Gas chromatogram of water extract of pyridazinones (1.69 mg of PCA per litre) on the column with 2% OV-17 on Chromaton N AW DMCS at 473°K and nitrogen pressure of 25.33 kPa; 500 ml of water sample was taken for extraction; 1.1 μl was injected from the final volume of 5 ml.

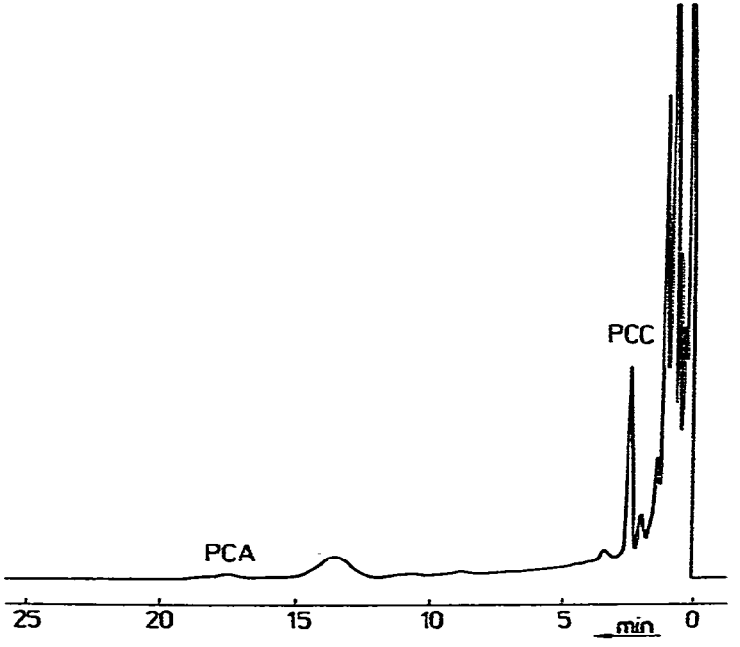


Fig. 2. Gas chromatogram of water extract of pyridazinones (4.37 mg of PCC per litre); 1.7 μl was injected from the final volume of 5 ml. The conditions were the same as in Fig. 1.

TABLE III

DETERMINED AMOUNTS OF PCA AND PCC IN WASTE WATERS

Sample	*PCA (mg/l)*	*PCC (mg/l)*
I	1.69 ± 0.18	4.37 ± 0.33
II	0.79 ± 0.09	4.49 ± 0.34

to determine whether there is a random or systematic error[13]. The limit of detection (3 × noise) of injected standard was found to be 30 ng of PCA and 1 ng of PCC; values of 6.6 μg of PCA per litre and 0.2 μg of PCC per litre were found when 1 l of water sample was extracted to a final volume of 0.2 ml.

The analysis of a practical sample of pyridazinones water extract is shown in Figs. 1 and 2. The amounts of PCC and PCA in waste waters, which represent the average values of three measurements, are given in Table III. In the quantitative analysis of practical samples, where besides the substances of interest there were many other compounds, the peak position was checked by the standard addition method. The GLC method was compared with high-performance liquid chromatographic method, where the possibility of the overlapping of a peak of interest was excluded by using many mobile phases of different polarity. The results of this part of the work are to be published elsewhere[13]. The results gained by both methods are in good agreement.

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