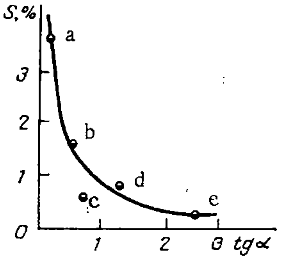

Fig. 4. Correlation relationship between mean square error S and tan α: a) I-II; b) VII-VIII; c) III-IV; d) V-VI at $pH \leq 2.0$; e) V-VI at $pH \leq 1.5$.

R, which corresponds to the composition of the sample, was found from the nomogram. A line parallel to the auxiliary lines was drawn through point R, the overall concentration of the solution was read from its intersection with the OA or OC axis, and a ray through point T was then drawn from the apex of the nomogram to the intersection with line AC, where the concentrations of the components of the mixture in percent were read.

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GAS-CHROMATOGRAPHIC ANALYSIS OF PYRIDINECARBOXYLIC ACIDS ON THE BASIS OF THEIR PYROLYSIS PRODUCTS

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The use of pyrolysis in gas chromatography has expanded its analytical potential and makes it possible to get a quicker solution to several complex analytical problems [1-3].

Here for analytical purposes we have examined the pyrolysis of pyridinecarboxylic acids (PCA) in the presence of nitrogen compounds that are capable on heating of decomposing and evolving ammonia or amide, imide, and other nitrogen radicals. The pyrolysis products are the pyridine bases (PB) and the nitriles of the corresponding PCA's. The cyanopyridines (CP) were identified from the IR spectra, melting point, and GLC (by retention times). For comparison of the retention times we used the CP's prepared by dehydration of the PCA amides with phosphorus pentoxide.

Pyrolysis was carried out in a Pyrex glass thimble (8-10 × 0.6-0.7 cm). Figure 1 shows the scheme of the setup and the order of filling of the thimble.

The quantity of the PCA was about 0.05 g (exactly weighed quantity). The standards were 2,4,6-collidine, 2,5-lutidine, quinoline, or PCA's other than the pyrolysis products (CP) from the analyte. The standard was added directly to the weighed quantity of the analytical PCA. The packing was powdered inorganic substances. All the components of the thimble contents

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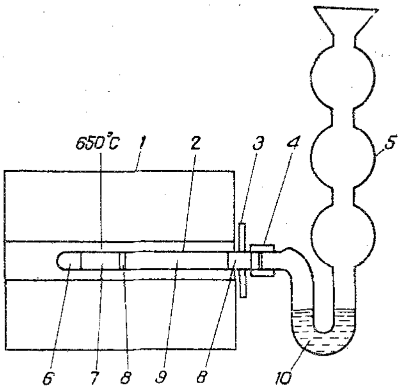

Fig. 1

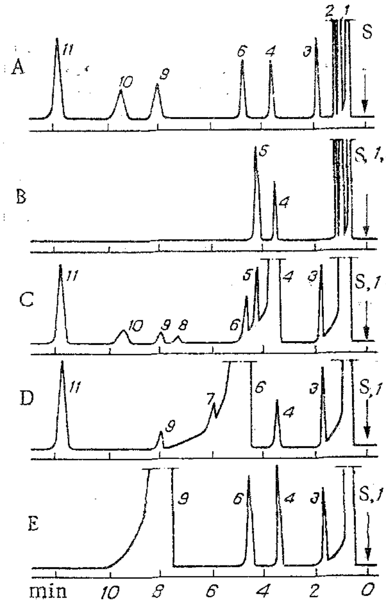

Fig. 2

Fig. 1. Setup for pyrolysis of PCA's: 1) tubular electric furnace (SUOL-0,15.06/12MR-IZ); 2) glass thimble; 3) Teflon washer; 4) rubber sleeve; 5) glass trap; 6) nitrogen compound (urea); 7) weighed quantity of PCA with standards; 8) glass fiber; 9) packing (powdered KSKG silica gel; 10) chloroform.

Fig. 2. Chromatograms of the pyrolysis products of urea with A) isonicotinic, nicotinic, picolinic, and 6-methylpicolinic acid; B) lutidinic and 2-methylisonicotinic acid; C) isonicotinic acid; D) nicotinic acid; E) picolinic acid; S) solvent (chloroform); 1) pyridine; 2) 2-methylpyridine; 3, 11) 2,4,6-trimethylpyridine and quinoline (standard substances); 4) 4-cyanopyridine; 5) 2-methyl-4-cyanopyridine; 6) 3-cyanopyridine; 7) 2-methyl-5-cyanopyridine; 8) unidentified; 9) 2-cyanopyridine; 10) 6-methyl-2-cyanopyridine.

were thoroughly compacted. A trap with 1-5 ml of chloroform was attached to the thimble with a rubber sleeve.

The trap, height 12-15 cm, was made from a glass tube of 0.8-1 cm diameter. The thimble was heated in an electric furnace at 600-650°C. The pyrolysis products (with the standards) were trapped in the trap with chloroform and then chromatographed.

We used an LKhM-8MD model 5 chromatograph (flame-ionization detector) with column (300 × 0.3 cm) packed with 1% $PEG_{300}C_2$ on Chromaton N-AW DMCS (0.16-0.20 mm) with 0.5% potassium hydroxide. The $PEG_{300}C_2$ stationary liquid phase was prepared in the plant laboratory by the method of [4, 5] on the basis of equimolar wuantities of polyethyleneglycol PEG-300 and sebacic acid (C_2).

The chromatograms (Fig. 2) were obtained at a column temperature of 110°C.

Dicyanopyridines (DCP) were chromatographed at 170°C. The flow rate of the carrier gas (nitrogen) was 60 ml/min, the injector temperature about 300°C. The order of elution of the monocyanopyridines (CP) could be found from the chromatograms (Fig. 2A, C, and D). The order of elution of the DCP's was 2.3-, 2,4-, 2,5-, and 2,6-DCP. The retention time of 2,6-DCP was 10 min. The complete separation of the nitriles on the columns with polyester stationary liquid phases was much easier than that of PB's and PCA esters and amides.

We chose the optimum conditions on the basis of analysis of 3-PCA nitrile (3-CP) in the pyrolysis of synthetic mixtures of 3-PCA with a standard (2,4,6-collidine) and the relative calibration coefficients (K).

We determined the yield of 3-CP by chromatographic analysis of the pyrolysis products of a synthetic mixture. We found K from the well-known equation [5] from the weight ratio of 3-

TABLE 1. Pyrolysis of Nicotinic Acid with Added Nitrogen Compounds (packing powdered KSKG silica gel G, grain size 0.00-0.25 mm)

Nitrogen compound	Yield of pyrolysis products, %	
	pyridine	3-cyanopyridine
No nitrogen compounds added	98,0	1,2
Sodium nitrite	24,4	5,3
Ammonia (25% aqueous solution)	50,7	7,7
Ammonium citrate	62,0	11,7
Ammonium perchlorate	67,1	22,1
Hydrazine sulfate	20,4	34,5
Phenylhydrazine base	32,1	66,1
Isonicotinic acid hydrazide	—	20,9
Metazid	—	16,5
Isoniazid	—	13,3
Isonicotinamide	—	26,4
Urea	0,4	93,0

TABLE 2. Pyrolysis of Nicotinic Acid in the Presence of Urea with Different Types of Packings

Packing	Yield of pyrolysis products, %	
	pyridine	3-cyanopyridine
Glass fiber	0,6	1,7
Sodium carbonate	40,0	19,8
Cupric oxide	77,8	8,7
Calcium oxide	27,2	36,7
Zinc oxide	28,2	49,7
Aluminum oxide	3,0	84,0
Microporous silica gel (MSA-2), powdered (0.00-0.25 mm)	0,7	72,5
Large-pore silica gel (KSKG), powdered (0.00-0.25 mm)	0,5	92,3

PCA and the standard in the mixture and the peak heights of the standard and 3-CP on the chromatogram of the pyrolysis products of the same mixture. The results of the pyrolysis of 3-PCA in the presence of different types of nitrogen compounds and using different types of packings are summarized in Tables 1 and 2. The yield of 3-CP was highest when 3-PCA was pyrolyzed in the presence of urea with powdered KSKG silica gel (grain size 0.00-0.25 mm) as packing. When used as nitrogenous additives in pyrolysis (Table 1) for the formation of 3-CP from 3-PCA, isoniazid, metazid, and other derivatives of isonicotinic acid (4-PCA), were themselves converted to 4-PCA nitrile (4-CP) and PB. The pyrolysis of the ammonium salt, hydrazide, amide, and hydroxymethylamide of 3-PCA also formed 3-CP in yields of 19, 35, 77, and 67% of the theoretical respectively (urea and other nitrogen compounds were not added in this case). This demonstrates that pyrolysis can also be used for the analysis of a number of PCA derivatives. The packings used during pyrolysis (Table 2) prevented sublimation of the PCA's, retained the resinification products in the thimble, and promoted a change in the direction of pyrolysis toward nitrile or PB formation. Of the compounds listed in Table 2, sodium carbonate was the best packing for the analysis of PCA's on the basis of their decarboxylation products [3]. Cupric oxide was converted into cuprous oxide in the pyrolysis of PCA's as a result of oxidation of the methyl groups of the methylpyridinecarboxylic acids and could therefore be used for the identification of these acids.

When the pyrolysis time of mixtures of 3-PCA with the standard 2,4,6-collidine and urea (10 mixtures) was changed from 1 to 10 min the average value of K was 3.04 ± 0.04. The average value of K found from 10 mixtures in which the weight ratio of urea to 3-PCA was varied from 0.7 to 3.0 was 3.04 ± 0.03. The constancy of K demonstrates that this method can be used for the quantitative determination of 3-PCA.

The results for 3-PCA were supported by analogous tests with 4-PCA.

In the determination of 4-PCA relative to 3-PCA the error of the method was ±5 rel.%; the number of mixtures was 12 and confidence level 95% (the experimental data were analyzed with the mathematical statistics of linear relations in terms of Student's coefficient [6, 7]). The error as a rule was lower in the determination of PCA relative to 2,4,6-collidine or quinoline.

Figure 2B shows the chromatogram of the pyrolysis products of a mixture of acids derived by refluxing 2,4-lutidine with formalin followed by oxidation of the methylol derivatives with nitric acid.

The chromatogram supports published work [3] on the site of formation of methylol groups in the pyridine ring when 2,4-lutidine is refluxed with formalin. The chromatograms (Fig. 2C, D, and E) demonstrate that pyrolysis in the presence of urea can be used for the analysis of impurities whose determination is difficult or impossible by other methods. The minimum amount of the impurity that can be determined in PCA samples was about $1 \cdot 10^{-4}$%. The total quantity of impurities in some laboratory samples of 3-PCA and 4-PCA (Fig. 2C and D) reached 3%.

No impurities in 4-PCA were detected after recrystallization from water. Samples of 2,6-pyridinecarboxylic acid were found to be contaminated by 3-PCA (0.01%). About 3% 4-PCA and about 4% 3-PCA (Fig. 2E) were detected in 2-PCA (technical sample).

The gas chromatographic analysis of PCA's on the basis of their pyrolysis products, the nitriles, can be used to determine almost any individual PCA's. Those PCA's whose nitrile pyrolysis products are different can be analyzed in mixtures. These include a number of their homologs and isomers. For example, all the components of mixtures consisting of different monopyridinecarboxylic acids can be determined.

Analysis by this method makes use of equipment, materials, and compounds that are common in chemical laboratories and plants. Changes in pyrolysis temperature and time and in the weight ratio of urea and PCA's are permissible within comparatively wide limits. Complete separation of the nitrile pyrolysis products is easily achieved on columns with NZhF polyester. The time required for analysis is short. All this makes this analytical method easily accessible for practical use in the laboratory of chemical plants.

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