Estimation of nitrogen functional groups by reaction gas chromatography — frontal technique Azoxy compounds, triazene and pentaza-1,4-diene derivatives

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A method of selective nitrogen determination was worked out for azoxy compounds, triazene and pentaza-1,4-diene derivatives; it is based on the destruction of the compounds in wet way with gas chromatographic determination of liberated elemental nitrogen by frontal technique. Decomposition of compounds proceeds in the apparatus placed in front of the chromatographic unit of the CHN-1 analyzer.

The worked out method makes the determination of nitrogen possible in separate functional groups giving reliable and exact results and extending application possibilities of the apparatus.

Разработан метод избирательного определения азота в азокси--соединениях, триазеновых и пентаза-1,4-диеновых производных, основанный на мокром разложении этих соединений и газово--хроматографическом определении выделяющегося элементарного азота фронтальным методом. Разложение соединений происходит в приборе, помещенном перед хроматографическим блоком анализатора CHN-1.

Разработанный метод позволяет проводить определение азота в различных функциональных группах и дает точные и надежные результаты, а также расширяет возможности применения прибора.

Nitrogen determination in organic compounds is an important component part of organic analysis. The classical methods can be divided into two major groups — universal methods (Dumas, ter Meulen) and selective methods which are applicable for certain functional groups (van Slyke). Introduction of gas chromatography into elemental analysis made possible simultaneous determination of several elements in the analyzed compounds. Application of thermal conductive detector did away with gravimetric and gasometric finish of the analysis.

Gas chromatography links up with the reaction process and represents a method enabling stepwise determination of separate functional groups present

either in organic or inorganic compound as well as partial automation of the whole process.

The present paper is aimed at determination of nitrogen in azoxy compounds and also in triazene and pentaza-1,4-diene derivatives, which have recently become the object of interest because of their chemical and biological effects, using frontal chromatography and elemental CHN-1 analyzer. It links up with the already described methods of nitrogen determination in azo compounds [1], hydrazine and its derivatives [2], ammonia salts, urea, nitrites, nitrates and fertilizers [3], and oximes, semicarbazones, nitroanilines, and amino acids [4].

Experimental

Apparatus

All the compounds were analyzed by the CHN-1 analyzer (Laboratorní přístroje, Prague) in which oxidation tube was replaced by reaction and sorption apparatus, the heating unit (Fig. 1).

The set up of individual parts of the apparatus and their link up as well as the determination method is described in detail in papers [1, 5—7].

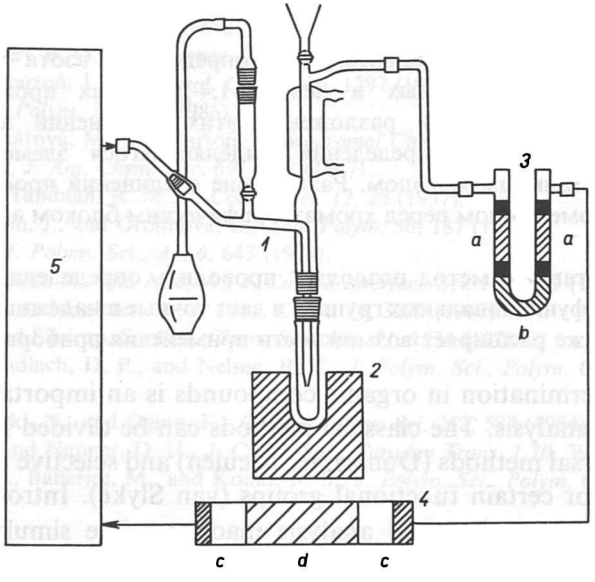

Fig. 1. Diagram of the apparatus for nitrogen determination.
1. Reaction apparatus; *2.* heating unit; *3.* sorption tube; *4.* reduction tube; *5.* pneumatic and chromatographic part of the analyzer.
a) Silica gel; *b*) ascarite; *c*) silver shavings; *d*) copper wire.

Compounds tested

Commercial or laboratory preparations were used. Their purity was checked up by means of the melting point and elemental analysis. The compounds are unambiguously determined by the group (table) number and ordinal number, *e.g.* 1/*I*.

Azoxy compounds: azoxybenzene (1/*I*), 4,4′-dimethylazoxybenzene (1/*II*), 4,4′-dimethoxyazoxybenzene (1/*III*), 4,4′-diethoxyazoxybenzene (1/*IV*), 4,4′-dibromoazoxybenzene (1/*V*), 4,4′-diiodoazoxybenzene (1/*VI*), 2,5,2′,5′-tetrachloroazoxybenzene (1/*VII*), 3,4,3′,4′-tetrachloroazoxybenzene (1/*VIII*).

Triazenes: 1-(4′-carboxyamidophenyl)-3,3-dimethyltriazene (2/*I*), 1-(2′-carboxyamidophenyl)-3,3-dimethyltriazene (2/*II*), 1-(4′-carboxymethylphenyl)-3,3-dimethyltriazene (2/*III*), 1-(3′-carboxyphenyl)-3,3-dimethyltriazene (2/*IV*), 1-(4′-carboxyphenyl)-3,3-dimethyltriazene (2/*V*), 1-(4′-methylphenyl)-3,3-dimethyltriazene (2/*VI*), 1-(2′-cyanophenyl)-3,3-dimethyltriazene (2/*VII*), 1-(4′-dimethylamino)-3,3-dimethyltriazene (2/*VIII*), 1-(2′-aminoacetophenyl)-3,3-dimethyltriazene (2/*IX*), 1-(4′-aminoacetophenyl)-3,3-dimethyltriazene (2/*X*), 1-(4′-aldehydephenyl)-3,3-dimethyltriazene (2/*XI*), 1-(4′-ethoxyphenyl)-3,3-dimethyltriazene (2/*XII*), 1-(4′-nitrophenyl)-3,3-dimethyltriazene (2/*XIII*), 1-(4′-iodophenyl)-3,3-dimethyltriazene (2/*XIV*), 1-(4′-chlorophenyl)-3-methyltriazene (2/*XV*), 1-(4′-bromophenyl)-3-methyltriazene (2/*XVI*), 1,3-bis(2′-chlorophenyl)triazene (2/*XVII*), 1,3-bis(3′-chlorophenyl)triazene (2/*XVIII*), 1,3-bis(4′-bromophenyl)triazene (2/*XIX*), 1,3-bis(4′-methylphenyl)triazene (2/*XX*), 1,3-bis(3′-methoxyphenyl)triazene (2/*XXI*).

Pentaza-1,4-dienes: 1,5-diphenyl-3-methylpentaza-1,4-diene (3/*I*), 1,5-bis(4′-chlorophenyl)-3-methylpentaza-1,4-diene (3/*II*), 1,5-bis(4′-bromophenyl)-3-methylpentaza-1,4-diene (3/*III*), 1,5-bis(4′-iodophenyl)-3-methylpentaza-1,4-diene (3/*IV*), 1,5-bis(4′-methylphenyl)-3-methylpentaza-1,4-diene (3/*V*). Working procedures are given with separate types of compounds.

Results and discussion

Determination of azoxy group

Eight compounds were analyzed by means of oxidative mineralization using chromic acid.

Three variants of the decomposition were used:

Procedure A: 2 cm^3 of concentrated sulfuric acid were added to the sample followed by 2 cm^3 of chromic acid ($c = 1.76$ mol dm^{-3}). Unless the sample liberated nitrogen quantitatively the opposite procedure *B* was used.

Procedure B: First 2 cm^3 of chromic acid ($c = 1.76$ mol dm^{-3}) were added to the sample and then 2 cm^3 of concentrated sulfuric acid. Unless the azoxy compounds reacted quantitatively in 20 min, the most pronounced procedure *C* was used.

Procedure C: 2 cm^3 of chromic acid ($c = 5.01\ mol\,dm^{-3}$) were added to the sample followed by 2 cm^3 of concentrated sulfuric acid. The weighed amounts were chosen so as to allow the nitrogen content to vary from 1 to 2 mg (10—20 mg of the compound). The calculation was carried out from calibrated dependence of azobenzene ($y = 209.46x + 0.262$; $s_{x,y} = 1.619$).

After the initial more violent reaction course, the reaction test tube was inserted into the heating unit (160 °C). After 10 min the helium flow was increased from 10 $cm^3\,min^{-1}$ to 30 $cm^3\,min^{-1}$, which means that the time for filling the diffusion cell (reaction time) was 20 min and the overall time of the analysis of one weighed amount was 30 min.

In procedure *A*, only compounds 1/*I*, *V*, *VI*, and *VII* liberated nitrogen quantitatively. The compound 1/*II* liberated about 50 %, 1/*III* 10 %, 1/*IV* 15 %, and 1/*VIII* 90 %. To the said compounds procedure *B* was applied — the compounds 1/*III* and *IV* reacted quantitatively; 1/*II* and *VIII* had about 90 % reaction. The latter substances were analyzed using procedure *C*. The liberated nitrogen was in good agreement with the theory. Lower yields during analysis of the compound 1/*II* using procedure *B* and of compounds 1/*VIII* using procedures *A* and *B* are due to the fact that these compounds are not ready to be wetted either with sulfuric or chromic acids. Crystals of the compound float on the surface of the reaction solution and the bubbles of the carrier gas carry them out of reach of the reaction mixture. More drastic conditions for decomposition were employed so that the time of analysis should not be extended.

It follows from the results obtained as well as from the statistical evaluation (Table 1) that the determination is exact, which is in good agreement with the work of *Jureček et al.* [8].

Table 1

Results of azoxy group determination given in mass %

Compound	Procedure	μ	$\bar{x}$	R	CI	s	u
I	*A*	14.13	14.21	0.36	14.21 ± 0.183	0.155	0.222
II	*C*	12.38	12.33	0.30	12.33 ± 0.152	0.129	0.166
III	*B*	10.85	10.86	0.46	10.86 ± 0.233	0.198	0.022
IV	*B*	9.78	9.80	0.16	9.80 ± 0.081	0.069	0.125
V	*A*	7.87	7.96	0.26	7.96 ± 0.132	0.112	0.346
VI	*A*	6.22	6.34	0.28	6.34 ± 0.142	0.120	0.429
VII	*A*	8.34	8.40	0.35	8.40 ± 0.177	0.150	0.171
VIII	*C*	8.34	8.28	0.47	8.28 ± 0.238	0.202	0.128

Determination of nitrogen in triazene derivatives

The decomposition of the substances tested in the apparatus (*1*) was carried out with two chromic acid concentrations in sulfuric acid medium.

In case the sample did not liberate nitrogen quantitatively using procedure *A*, procedure *D* was employed.

Procedure D: The acids are dosed in the reversed order than in procedure *C*, *i.e.* first 2 cm^3 of concentrated sulfuric acid followed by 2 cm^3 of chromic acid ($c = 5.01\ mol\,dm^{-3}$).

The weighed amounts of the standard (azobenzene) as well as of compounds being tested were selected so that the nitrogen content could vary from 1 to 4 mg (5—30 mg of the compound).

Working conditions are identical with those employed in determination of the azoxy group.

During oxidative mineralization with chromic acid, two thirds of nitrogen of triazene group pass on the elemental nitrogen, the rest passing on to ammonia, or methylamine or dimethylamine. This decomposition is convenient for —N=N— determination in triazene derivatives using reaction gas chromatography.

Table 2

Results of triazene derivatives determination given in mass %

Compound	Procedure	μ	$\bar{x}$	R	CI	s	u
I	*A*	14.57	14.54	1.67	14.54 ± 0.848	0.718	0.018
II	*A*	14.57	14.49	0.32	14.49 ± 0.162	0.138	0.250
III	*B*	13.52	13.29	1.08	13.29 ± 0.548	0.464	0.213
IV	*B*	14.50	14.27	0.46	14.27 ± 0.117	0.099	0.500
V	*A*	14.50	14.87	1.02	14.87 ± 0.517	0.439	0.363
VI	*A*	17.16	17.12	0.41	17.12 ± 0.208	0.176	0.098
VII	*A*	16.08	16.19	0.28	16.19 ± 0.142	0.120	0.393
VIII	*A*	14.57	14.32	1.36	14.32 ± 0.690	0.585	0.184
IX	*A*	13.52	13.58	0.42	13.58 ± 0.213	0.181	0.143
X	*A*	13.52	13.60	0.49	13.60 ± 0.248	0.211	0.163
XI	*A*	15.81	15.83	0.60	15.83 ± 0.304	0.258	0.033
XII	*A*	14.50	14.46	0.35	14.46 ± 0.177	0.151	0.114
XIII	*D*	14.43	10.73	1.03	10.73 ± 0.522	0.443	3.592
XIV	*A*	10.18	10.21	0.07	10.21 ± 0.035	0.030	0.429
XV	*A*	16.52	16.53	0.48	16.53 ± 0.243	0.206	0.021
XVI	*A*	13.09	12.93	0.47	12.93 ± 0.238	0.202	0.340
XVII	*D*	10.53	5.16	0.41	5.16 ± 0.208	0.176	13.098
XVIII	*A*	10.53	10.65	0.62	10.65 ± 0.314	0.267	0.194
XIX	*D*	7.89	5.59	5.73	5.59 ± 2.905	2.464	0.401
XX	*A*	12.43	12.31	1.42	12.31 ± 0.720	0.611	0.085
XXI	*A*	10.89	10.93	0.29	10.93 ± 0.147	0.125	0.138

The results of analyses carried out in 21 compounds tested were summed up in Table 2; they are well reproducible and, excepting negatively substituted derivatives, they are not loaded with a systematic error. The negative group stabilizes the molecule towards the attack by the reagent. The compounds 2/*III*, *IV*, *XIII*, *XVII*, and *XIX* gave under standard conditions of oxidation (procedure *A*) low yields. In a more radical degradation (procedure *D*), the compounds 2/*III* and *IV* gave off nitrogen quantitatively and the results were correct. On the other hand, compounds 2/*XIII*, *XVII*, and *XIX* under identical conditions, gave only 50—70 % of the theoretical nitrogen amounts. In arylmethyl- and aryldimethyltriazenes (without negative groups on the nucleus), nitrogen development was very rapid. It started without being heated on adding concentrated sulfuric acid to the sample and ended in 5—7 min, which enabled to shorten the time for one analysis to 15 min. Protolysis of triazene derivatives with diluted mineral acids, on the basis of identification with decomposition products and kinetic measurements, was systematically studied by *Matrka et al.* [9]. The mechanism of decomposition with sulfuric acid under increased temperature was formulated by *Jureček et al.* [10].

Nitrogen determination in pentaza-1,4-diene derivatives

Decomposition in the apparatus (*1*) was carried out with chromic acid in sulfuric acid medium (procedure *A*) or concentrated sulfuric acid (procedure *E*).

Procedure E: The compound being tested was heated with only concentrated sulfuric acid (4 cm^3).

As standard for calculation, azobenzene (decomposed with chromic acid) was used, the weighed amounts ranging from 5—15 mg. Working conditions are similar to those used with azoxy compounds, helium flow 20 $cm^3 min^{-1}$ taking 20 min.

Results of analyses of five compounds tested are arranged in Table 3. They are well reproducible and without systematic error. Decomposition with sulfuric acid gave identical results as that with chromic acid. Nitrogen development was rapid, the results corresponded to theory, the errors of separate determinations did not exceed ± 0.3 % abs. This procedure represents an alternative procedure of nitrogen determination in diarylmethylpentazadienes and, if combined with chromic acid decomposition, enables their differentiation from the compounds containing isolated —N=N— groups.

In oxidative mineralization of 1,5-diaryl-3-methylpentaza-1,4-dienes, four fifths of nitrogen of pentazadiene group pass on to elemental nitrogen, the rest passing on to methylamine. Reaction mechanism of protolysis of pentazadiene derivatives of concentrated sulfuric acid under elevated temperature was worked out by *Jureček et al.* [10].

Table 3

Results of pentaza-1,4-diene derivatives determination given in mass %

Compound	μ_{azo}	Procedure *A*					Procedure *E*					$u_{A,E}$
		$\bar{x}_A$	R_A	CI_A	s_A	u_A	$\bar{x}_E$	R_E	CI_E	s_E	u_E	
I	23.42	23.44	0.19	23.44 ± 0.096	0.082	0.105	23.45	0.38	23.45 ± 0.193	0.163	0.079	0.018
II	18.18	18.15	0.19	18.15 ± 0.096	0.082	0.158	18.19	0.21	18.19 ± 0.107	0.090	0.048	0.100
III	14.11	14.10	0.39	14.10 ± 0.198	0.168	0.026	14.07	0.53	14.07 ± 0.269	0.228	0.076	0.033
IV	11.41	11.43	0.30	11.43 ± 0.152	0.129	0.067	11.42	0.32	11.42 ± 0.162	0.138	0.031	0.016
V	20.96	20.91	0.23	20.91 ± 0.117	0.099	0.217	20.88	0.26	20.88 ± 0.132	0.112	0.308	0.061

Number of determinations $n = 5$; μ, $\bar{x}$ – theoretical and average values of nitrogen content; R — variation range ($R = x_{max} - x_{min}$); CI — confidence interval ($CI = \bar{x} \pm K_n R$); s — standard deviation ($s = k_n R$); u — Lord's coefficient ($u = |\mu - \bar{x}|/R$). Tabulated values of coefficients ($\alpha = 0.05$); $K_5 = 0.507$; $k_5 = 0.430$; $u_0 = 0.507$; $u_{A,E} = 0.306$.

Conclusion

A modern analytical method was worked out to determine nitrogen functional groups using reaction gas chromatography, which can replace the classical procedures so far in use. It enables simplification of apparatus arrangement and partial automation of the whole process. The time for one analysis (limited by decomposition time) is, if compared with the methods using combustion, not convenient but, in view that it enables nitrogen determination in separate functional groups, is acceptable. Adaptation of the CHN-1 analyzer is quick, not costly, meeting the demands of laboratory practice and considerably extends the application of the apparatus.

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