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UTILIZATION OF THE FRONTAL TECHNIQUE IN REACTION GAS CHROMATOGRAPHY FOR THE DETERMINATION OF FUNCTIONAL GROUPS

DETERMINATION OF AN AZO GROUP

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SUMMARY

The determination of an azo group by means of reaction gas chromatography was studied, utilizing frontal chromatographic separation. A reactor, inside which elemental nitrogen was liberated from azo compounds by oxidative fission with chromic acid, was installed in the elemental analyser. The elemental nitrogen was determined from the step height in the frontal gas chromatogram.

INTRODUCTION

The determination of nitrogenous functional groups in organic compounds can be carried out by means of universal methods (elemental analysis) on the one hand, and by means of methods that can be used for certain functional groups (functional analysis) on the other. Elemental analysis by means of reaction gas chromatography (GC) can be classed with universal methods. A number of commercial elemental analysers based on GC have been developed, and various methods of reaction GC¹ utilizing suitable chemical reactions have also been devised for the determination of nitrogenous functional groups. This reaction is carried out in a reactor installed within the GC system.

In recent years, we have been developing methods for the determination of some nitrogenous functional groups by means of reaction elution GC²⁻⁶. Organic compounds with different functional groups were degraded in the reactor by means of chosen oxidative agents. The gaseous products of the fission were carried by a stream of carbon dioxide into a reservoir that was part of the by-pass gas dosing device of a commercial gas chromatograph. After completion of the chemical reaction, the contents of the reservoir were subjected to chromatographic analysis.

We are studying the utilization of reaction GC with the frontal technique for the determination of functional groups. For this purpose we have applied the elemental analysis of carbon, hydrogen, nitrogen and possibly oxygen in organic compounds⁷⁻⁹. This method utilizes the frontal chromatographic separation of combustible products (carbon dioxide, water, nitrogen and possibly carbon monoxide) after their dilution with the carrier gas and establishment of diffusion equilibrium. A certain functional group can be determined selectively by installing the reactor in the analyser system and by carrying out a suitable chemical reaction. Fission of nitrogenous compounds by chromic acid had earlier been shown to be an efficient method in connection with the classical gas measurement method for the determination of nitrogen in N-N bonds and has been studied thoroughly by Jureček and co-workers^{10,11}. In this paper, a process for the determination of an azo group by means of reaction frontal GC after oxidative fission of the compound by chromic acid is described.

EXPERIMENTAL

Test substances

The following commercial or synthesized compounds were used, their purities being established by determination of their melting points and by elemental analysis: 4-methylazobenzene (I), 4-aminoazobenzene (II), 4-hydroxyazobenzene (III), 4-ethoxyazobenzene (IV), 4-N,N-dimethylaminoazobenzene (V), 1-(phenylazo)-2-naphthol (VI), 4'-nitro-2,4-dihydroxyazobenzene (VII), 1-(4-methylphenylazo)-2-naphthol (VIII), 4'-N,N-dimethylaminoazobenzene-2-carboxylic acid (IX), 4'-N,N-dimethylamino-2,4-diaminoazobenzene (X) and 4'-N,N-dimethylaminoazobenzene-4-sulphonic acid (XI).

The standard used was azobenzene.

Equipment

Fig. 1 shows the assembled equipment. A CHN-1 elemental analyser (Laboratory Instruments, Prague, Czechoslovakia) (Fig. 1A) was used. Its main components are a sample dosing device, a reaction section consisting of an oxidation-reduction combustion tube made of quartz-glass and the so-called analytical section. The latter part consists of a temperature-controlled oven in which are situated the dilution cell (15), a chromatographic column (14) and a kathorometer (16).

A reactor with a sorption U-tube (Fig. 1B) was installed in the pneumatic circuit in front of the reduction tube. In contrast to the standard connection used in elemental analysis^{7,8}, it was not necessary in this instance to connect an oxygen source, or to use a sample dosing device and an oxidation tube. In addition to the TZ 211S recorder (Laboratory Instruments) (17), an NR 50 digital voltmeter together with a Z 37 amplifier (both from Metra Blansko, Czechoslovakia) (20) were connected in parallel to the analyser. The sorption U-tube was filled with silica gel in the arms (11) and askarite at the bottom (12). The oxidative mixture in the reaction test-tube (2) was heated with the aid of an aluminium electrical heating block (8), the input of which was regulated by an autotransformer (9).

Operating conditions

A 1.3 m × 3 mm I.D. stainless-steel column filled with molecular sieve 5A

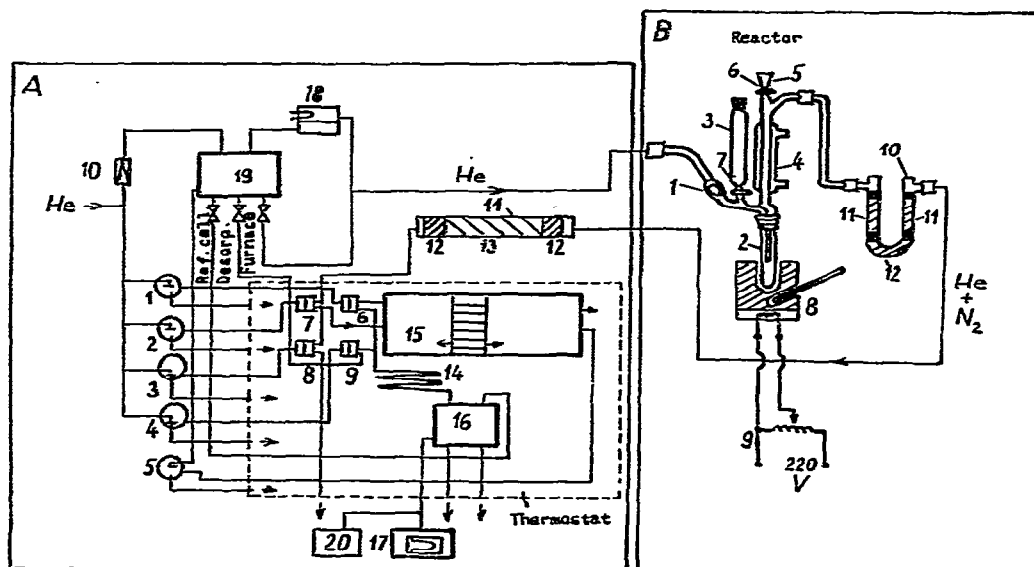


Fig. 1. Diagram of equipment. (A) The utilized part of the CHN-1 elemental analyser. 1-5 = Solenoid valves; 6-9 = diaphragm-operated valves; 10 = pressure-reducing valve; 11 = reduction tube; 12 = silver shavings; 13 = copper wire; 14 = chromatographic column; 15 = dilution-type cell; 16 = katharometer; 17 = recorder; 18 = manometer; 19 = pressure reservoir; 20 = digital voltmeter. (B) Connected reactor and sorption U-tube. 1 = Ground check-valve; 2 = reaction test-tube; 3 = reservoir for oxidation reagents; 4 = reflux condenser; 5 = funnel; 6, 7 = simple taps; 8 = heating block; 9 = autotransformer; 10 = sorption U-tube; 11 = silica gel; 12 = askarite.

(40-80 mesh) (Carlo Erba, Milan, Italy) was used. The temperature of the chromatographic column, the dilution-type cell and the katharometer was 75°. Helium was used as the carrier gas. The reduction tube (Fig. 1A, 11) filled with silver shavings (12) and copper wire (13) was heated at 550°. The flow-rate of the carrier gas was 10 ml/min in the first half of the oxidative fission process, then it was increased to 30 ml/min; the flow-rate through the reference cell of the katharometer was 13 ml/min.

Procedure

A 10-15-mg amount of an azo compound was subjected to oxidative fission in the reactor by using 5 *N* chromic acid in 50% (v/v) sulphuric acid at 160° for 20 min. Under these conditions, elemental nitrogen was liberated and carried by the carrier gas through the U-tube and reduction tube into the dilution-type cell, where it was collected. Then the dilution-type cell closed automatically and, after stabilization of diffusion equilibrium (2 min), part of its contents was transferred to the chromatographic column for frontal separation and into the katharometer. The nitrogen content of the azo compound was determined with the aid of a standard.

The detailed procedure was as follows. The equipment was deaerated before beginning a daily series of analyses. After washing the apparatus, first 2 ml of concentrated sulphuric acid were added from the reservoir (Fig. 1B, 3) and, after dilution, the same volume of 5 *N* chromic acid was added. A small amount of both

sulphuric and chromic acids must always remain above the inlet cock (7) in order to avoid penetration of air into the system. After adding the chromic acid, the analyser functions automatically. After the initial spontaneous fission, the reaction test-tube was heated by the aluminium heating block at 160° for a chosen reaction period. Volatilization of some components of the mixture from the reaction test-tube is prevented by a water-cooled reflux condenser (Fig. 1B, 4). Acidic gaseous products and water that remained uncondensed were trapped imperfectly, so one part of the reduction tube (Fig. 1A, 11) was filled with silver shavings. A small amount of elemental oxygen liberated by the decomposition of chromic acid was removed by copper wire in the reduction tube, so that only elemental nitrogen was collected in the dilution-type cell.

The oxidation fission took place during the first 10 min with a flow-rate of the carrier gas of 10 ml/min followed by a further 10 min at 30 ml/min. After this period, the pressure in the dilution-type cell increased to 0.0775 MPa (0.8 kp/cm²) and it was then automatically shut. During the following 2 min diffusion equilibrium was established under constant conditions, then the contents of the dilution-type cell were purged for 3 min through the chromatographic column into the katharometer. During this period, frontal gas chromatographic separation took place in the column. After the passage of nitrogen, a stream of pure carrier gas was passed through and desorption of the column took place.

The height of the frontal chromatographic wave of nitrogen corresponds to the concentration of nitrogen in the dilution-type cell and thus also to the content of nitrogen in the azo compound. This height was read both from the chromatographic record and the digital voltmeter.

During the diffusion and adsorption periods, the reactor was prepared for the next analysis. Before adding the reagents to the substance being analysed, the flow-rate of the carrier gas was again reduced to 10 ml/min. The period required for one analysis is 25 min.

Calculation

The nitrogen contents of the azo compounds were calculated by means of a calibration graph constructed from the analysis of the standard (azobenzene). The standard was analysed at intervals in the daily series of analyses of samples. Within the range of nitrogen contents to be determined, the dependence of the height of its frontal wave (h mm) on the nitrogen content of the substance being analysed (x mg) is expressed by the straight line $h = ax + b$, where a is the slope of the line and b is the intercept on the h axis. This equation was determined for the standard from experimental values h_i and known values x_i by means of regression analysis. Contents of nitrogen, x_j , in the substances being analysed were calculated from the heights of the frontal curves and the determined coefficients a and b . The values obtained were converted into percentage nitrogen contents in the azo compounds and were used for statistical treatment. Each azo compound was analysed seven times. The result of the blank experiment was obtained in the same way and under the same conditions as during the determination itself.

RESULTS AND DISCUSSION

The results of the determination and the statistical evaluation are shown in Table I. The experimentally determined values of the nitrogen contents correspond to the theoretical values and the error of the determination is less than $\pm 0.3\%$ absolute. The calculated confidence interval, the standard deviations and their evaluation by means of the Lord test show that the method is reliable, has good reproducibility and has no systematic error (Lord's coefficient u is always less than the critical value u_0 tabulated for seven determinations and chosen as 0.05).

TABLE I

RESULTS OF THE DETERMINATION OF AN AZO GROUP

Number of determinations (n) = 7; μ , \bar{x} = theoretical and average values, respectively, of nitrogen contents; R = variation interval ($R = x_{\max} - x_{\min}$); IS = confidence interval ($IS = \bar{x} \pm K_n R$); s = standard deviation ($s = k_n R$); u = Lord's coefficient ($u = [\mu - \bar{x}]/R$). Tabulated values of coefficients: $K_7 = 0.33$; $k_7 = 0.37$; $u_0 = 0.333$.

Substance	μ (%)	\bar{x} (%)	R	IS	s	u
I	14.28	14.26	0.49	14.26 \pm 0.162	0.181	0.041
II	14.20	14.12	0.50	14.12 \pm 0.165	0.185	0.160
III	14.13	14.11	0.55	14.11 \pm 0.181	0.203	0.036
IV	13.32	13.25	0.47	13.25 \pm 0.155	0.147	0.149
V	12.47	12.40	0.33	12.40 \pm 0.109	0.122	0.121
VI	11.28	11.35	0.48	11.35 \pm 0.158	0.178	0.146
VII	10.85	10.78	0.55	10.78 \pm 0.181	0.203	0.127
VIII	10.68	10.68	0.48	10.68 \pm 0.158	0.177	0
IX	10.40	10.28	0.40	10.28 \pm 0.132	0.148	0.300
X	9.89	9.82	0.35	9.82 \pm 0.115	0.129	0.200
XI	9.18	9.19	0.34	9.19 \pm 0.112	0.126	0.029

Positive errors arise most frequently owing to the penetration of air into the system. Negative errors are caused by leakages or adherence of substance on the walls of the reaction test-tube out of reach of action of the oxidation mixture.

The determination of an azo group in this equipment can also be performed with smaller samples. It is also possible to set a lower value of the overpressure necessary for the automatic closure of the dilution-type cell. If a substance contains several different nitrogenous functional groups, it is possible to determine in the elemental analyser the total nitrogen content and, after installing the reactor, to determine selectively the azo group.

It follows from the results obtained that the determination of functional groups can usefully be carried out by reaction gas chromatography with the frontal technique. All chemical reactions that provide stoichiometric gaseous reaction products can be used. It is significant that these reactions need not take place instantaneously but can have a certain time course.

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