ACTA UNIVERSITATIS LODZIENSIS
FOLIA CHIMICA 13, 2004

OUTLINE OF CHN ELEMENTARY AND CN ENVIRONMENTAL ANALYSIS

by Zbigniew H. Kudzin* and Bogdan Waśkowski

University of Łódź, Institute of Chemistry, 68 Narutowicza Str.,
91-360 Łódź, Poland

A review on the CHN analysis of organic compounds and the CN environmental analysis is described. The review contains outline of the evolutionary development of elementary analysis, since Gay-Lussac, Dumas and Liebig era until a present state analysis, with computer controlled, fully automated analyzers. Physical principles of high temperature and low temperature combustions are discussed. Technical foundations on conjunctions of the high temperature combustion with chromatographic separations of the ultimate combustion products of organic samples, is delineated. Commercially available elemental analyzers are compared and their construction and operating principles are described. The basic methods of determination of environmental carbon and nitrogen are discussed. The representative analyzers for environmental carbon and nitrogen analysis are presented and their operating principles are described.

Key words: elementary analysis, simultaneous CH and CHN determinations, high temperature combustion, low temperature combustion, combustion products, gas chromatographic separation, thermal conductivity detection, infra-red detection, chemiluminiscence detection, microcoulometric detection, elemental analyzers, environmental analysis.

1. Outline of History of Elementary Analysis Development

A fast development of the organic chemistry in XX age was a result of earlier accomplishments on ground of elementary analysis of organic compounds. The first quantitative analysis of organic compounds (determinations of carbon and hydrogen) was elaborated by Gay-Lussac and Thenard, in 1805-1815 [1,2]. The determination was carried out in an apparatus an ideological scheme of which is illustrated in Fig. 1.

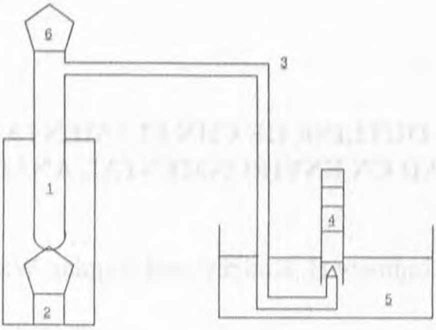


Fig. 1. Ideological scheme of apparatus to elementary analysis (C,H) of organic compounds by Gay-Lussac and Thenard:
1 – combustion tube; 2 – spirit lamp; 3 – pipe connecting the combustion tube with calibrated cylinder; 4 – calibrated cylinder; 5 – dish with mercury; 6 – lock of the combustion tube.

Analysis: a sample (**S***: 1-5 g) was mixed with perchlorate, placed into the combustion tube 1, and heated for the full thermal-oxidative degradation (scheme 1) of the compound analyzed. The combustion products - carbon dioxide, aqueous vapor, and derived from decomposition of perchlorate oxygen (scheme 1), were collected in the graduated cylinder 4, sealed hydraulically by means of mercury.

$$S^{*}\ (C_xH_{2y}O_z) \xrightarrow{KClO_3} x\,CO_2 + y\,H_2O + O_2$$

Scheme 1

The analysis of the gaseous combustion products, was labor-consuming and led to charged with considerable errors results.

The method of analysis providing far more accurate results on the determination of carbon and hydrogen was elaborated by Berzelius in 1814-1817 [385]. The method of Berzelius, considered as the real creator of the elementary analysis, depended on "the combustion" of a substance sample on the way of thermally induced reaction with potassium chlorate and the sequent gravimetric determination of formed water steam (increase of the mass of water absorber charged with anhydrous calcium chloride) as well as carbon dioxide (increase of the mass of carbon dioxide absorber, charged with potassium hydroxide).

Joseph L. Gay-Lussac (1778-1850)

Jean A. Dumas (1809-1884)

A considerable improvement of the method of carbon and hydrogen determination, was achieved with the work of Liebig, who in 1831 published the procedure differing fundamentally from methods of Gay-Lussac - Thenard and Berzelius. The combustions, Liebig carried out in an air atmosphere using copper oxide as the oxidant, in the apparatus schematically presented in Fig. 2. In this, Liebig applied for the combustion copper oxide (scheme 2), a new type of the combustion tube 1, and to heating the coal permissive on a zone heating furnace 3 [4,5].

$$S^* (C_xH_{2y}O_z) \xrightarrow[\text{Temperature}]{\text{CuO}} x\,CO_2 + y\,H_2O$$

Scheme 2

A special shape of the combustion tube (situated horizontally and sealed on one end) permitted after the combustions to rinse the tube with an air-stream, in order to achieve the quantitative absorption of the combustion products in the absorbers 5 - for water vapor (determined gravimetrically) as well as the 6 – for carbon dioxide (determined alkacimetrically). An ideological scheme of the apparatus of Liebig is presented in Fig. 2.

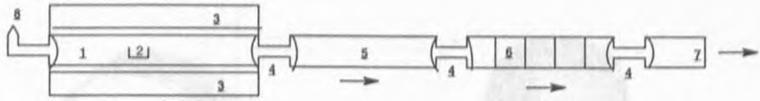


Fig. 2. Ideological scheme of the apparatus of Liebig for determination of carbon and hydrogen: 1 – combustion tube; 2 – porcelain boat to placing mixture of substance and oxidant; 3 – coal oven to zone heating; 4 – link; 5 – water vapor absorber ($CaCl_2$); 6 – carbon dioxide absorber (a ball absorber filled with solution of potassium hydroxide); 7 – outlet of the apparatus (connection with vacuum); 8 – end of the combustion tube, broken off after combustion with aim of washout of the combustion products passed in an air stream through absorbers.

The apparatus of Liebig, requiring for the analysis at least 0.2 g quantities of analyzed substance, made possible the analysis of new organic compounds on mass scale and played in the development of organic chemistry the significant part [385]. The apparatus of Liebig was applied widely by many decades without substantial principle changes.

Jons J. Berzelius (1779-1848)

The modifications, introduced successively concerned the construction of a furnace for combustions mainly, the way of heating of the combustion tube, and some details, influencing, however, the precision of determination. The essential modification of the apparatus of Liebig was introduced in 1870 by Lowe [10], who applied for combustions the tube bipartitely open. The method which introduction caused essential improvements in the CH determination, was elaborated by Dennstedt [17]. Dennsted carries out the combustion in the tube devoid of solid oxidative fillings. The combustion was carried out in the oxygen atmosphere, in a presence of the platinum catalyst (scheme 3).

$$S^{*}\ (C_xH_{2y}O_z) \xrightarrow[\text{Temperature}]{O_2\,/\,Pt} x\,CO_2 + y\,H_2O$$

Scheme 3

The apparatus of Dennstedt facilitated the simultaneous carbon and hydrogen determination, and additionally, made possible the determinations of sulfur and halogens, which were impossible in the apparatus of Liebig.

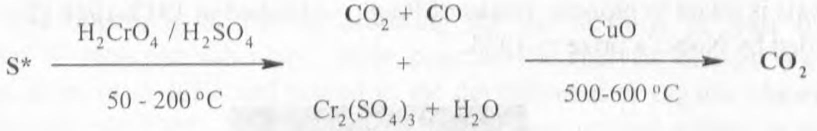
The paradigm from the gram to milligram scale in the elementary analysis is owed to pioneer works of Pregl, published in 1912-1916 [25,28] and awarded by Nobel's prize in 1923.

Fritz Pregl (1869-1930)

The results of works of Pregl (the mass of analyzed substance in a range 5-10 mg at error 0.3 %), consisted not only the largest achievement in the field of elementary analysis from the time of Liebig, but also a mile-stone event in the history of organic chemistry development, especially in chemistry of natural products.

In 1890, Messinger [15] elaborated depending on so called "wet combustion" the method of analysis of organic compounds, which permitted on the carbon determination in explosives as well as organometallic compounds and also salts, that is, the compounds which combustion on the "dry" way, was not possible. The method of Messinger, was based on the combustion of organic substance occurring during heating in a mixture of sulfuric and chromic acid. Because products of the reaction contained carbon monoxide (scheme 4), the re-oxidation of the formed gas products was necessary, achieved by the passage through a layer of glowing-hot copper oxide.

In the modifications made by Van Slyke and Folch [83,104,134,135], Mc Cready and Hassidy [91], and also by Binkowski [271], to "wet" combustions, an addition of iodic and chromic acids into a mixture of sulfuric and phosphoric acids, were applied. Formed quantitatively from the organic carbon of the sample carbon dioxide, it was then determined manometrically [37,105], gravimetrically [91,109] or alkacimetrically [115].



Scheme 4

Bobrański introduced in 1928 a speed combustion automatic regulation [43], preventing overheating of the combusted substance, and so eliminating too quick evaporation or decomposition of the substance in the combustion tube, the cause of incomplete combustions or explosions. In 1961, Ingram worked out the method of instant combustion (*flash combustion*) of organic compounds, depending thereon, that an analyzed substance is mixed with an oxidant in a foil metal capsule (foil of Al, Ag, Sn or Cu) and the capsule is introduced into the combustion tube (situated perpendicularly) [206]. During the combustion, the metallic capsule undergoes the oxidation, elevating considerably the combustion temperature (a few hundreds degree over temperature of the tube), which favours a quick and total combustion of the substance.

The endeavor to improvement of the methods of elementary analysis, concerned tests of render independent from the operator's manual predispositions analyze mainly, in majority, in the direction of automation. As a result, it was published in hundreds of works within the topic of elementary analysis, in this 1289 papers quoted in the handbook of quantitative analysis of organic compounds written by Bobrński [385], and edited in 1979. More advanced modifications depended on the utilization for heating of a boat with combusted substance by means of electric high-frequencies currents furnace [167], as well as further innovations applied in the combustion control [193,198].

On special attention deserve the methods of combustion carried out in an empty quartz tube at temperature 800-1100 °C, with the speed of the oxygen stream – 10-fold higher than in the classic method of Pregl [385], introduced in 1940-thies by Belcher [74-76] and Titov [82], as well as applied by another explorers [238,276]. The evolution of construction of the combustion tube in the last two centuries was presented recently by Burns [465].

In addition to above described methods - called dynamic and characterized by a continuous movement of gases inside an apparatus during the combustion, static methods were also introduced. In these, the combustion is carried out in a closed space in an oxygen atmosphere and/or by means of added to the substance some type of oxygen donors (solid oxidants). An instant combustion presents a special variant of combustion, introduced to microanalysis by Ingram [206], and adopted by other explorers [209,236,242, 260,287,347,463].

In the modification carried out by Kozłowski - called "ignition mineralization", the instant combustion was applied, for mixtures of oxidant and analyzed substance [326,331]. In this case, the combustion is partially and therefore obtained products of incomplete combustion (CH_4, CO) are necessary to convert quantitatively to carbon dioxide, prior to their final determination. This is achieved by the passage of formed fumes in a mixture with oxygen, through layers of oxidants and/or catalysts.

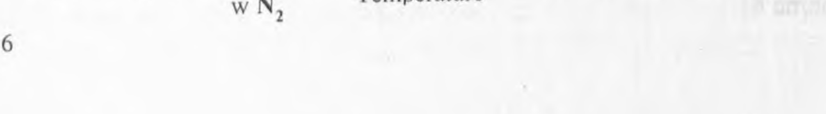
At present, the carbon determination in samples of diverse origin, in these in chemical substances, biological materials and/or in environmental samples, can be achieved by the use of a wide spectrum of commercially accessible carbon analyzers [440] and/or automatic CHN analyzers [385,440].

The first method of the quantitative nitrogen determination in organic compounds, was elaborated in 1831 by Dumas [3], and applied the combustion of mixtures of analyzed substances with copper oxide, inside the combustion tube in a carbon dioxide atmosphere (scheme 5).

$$S^* (C_xH_{2y}N_zO_m) \xrightarrow[\text{Temperature}]{CuO / CO_2} x\,CO_2 + y\,H_2O + z_{/2}\,N_2$$

Scheme 5

Dumas placed in the combustion tube a copper metallic layer, reducing formed during combustion nitrogen oxides to molecular nitrogen, determined subsequently in an eudiometer (azotometer) filled with an aqueous solution of potassium hydroxide (scheme 6).



$$x\,CO_2 + y\,H_2O + \substack{m\,NO_n \\ \\ w\,N_2} \xrightarrow[\text{Temperature}]{} x\,CO_2 + y\,H_2O + z_{/2}\,N_2$$

Scheme 6

Here, carbon dioxide underwent chemisorption; so a volumetric measurement of coming into the azotometer gas, afforded directly the volume of formed in the combustion nitrogen, and on this way the nitrogen content (scheme 7).

$$x\,CO_2 + y\,H_2O + z_{/2}\,N_2 \xrightarrow{KOH_{aq}} z_{/2}\,N_2$$

Scheme 7

The method of Dumas, after numerous modifications and adaptations in centigram, milligram and microgram (6,25,28,385) scales, constitutes to today the basic method of nitrogen determination in solid substances.

Kjeldahl, in 1883, described a straight line method of nitrogen determination in organic substances, depending on the mineralization of a sample by heating it in sulfuric acid [13]. In process of the mineralization, the "organic nitrogen" underwent to ammonium sulfate quantitative conversion, followed by the determination of ammonia, usually after its release by alkalization.

Kirsten, in 1946, introduced the combustion in a quartz tube at temperature 1050 °C [107]. To oxygenation of organic compounds he applied nickelous oxide (NiO), meanwhile nickel to the reduction of nitrogen oxides instead of metallic copper was used [123,124]. Schoniger introduced dry combustion of organic samples in an oxygen atmosphere and in the presence of platinum catalyst [164,176,192].

$$\begin{array}{lll} & H_2SO_4 \longrightarrow & \mathbf{BaSO_4} \\ S^* \xrightarrow[T > 100^{\circ}C]{HNO_3} & X_2 \longrightarrow & 2\,\mathbf{X}^- \\ & H_3PO_4 \longrightarrow & (NH_4)_3PO_4(MO_3)_{12} \end{array}$$

Scheme 8

Carius, in 1860-1865, introduced a classic method of determination of sulfur [7], halogens (Cl_2, Br_2, I_2) as well as phosphorus [9]. He carried out the mineralization by heating of samples in a concentrated nitrogenous acid under elevated pressure (sealed ampoule).

The microanalytical modifications of Carius procedure, accomplished by Emich and Donau [21], as well as others [385], find the use to nowadays (scheme 8).

Baubigny and Chavanne [19] worked out the method of mineralization of halogeno-organic compounds in a mixture of concentrated sulfuric and chromic acids, Volhard [11] applied the fusion of analyzed substances in mixtures with sodium carbonate and potassium nitrate, Pringsheim [20] in sodium peroxide. Kekule [8] halogen splintered off in result of the reduction with soda amalgam. The numerous modifications of above mentioned methods [79,118,158], as well as the present methods of determination of sulfur, phosphorus and halogens, were discussed in the review work of Bobrański [385].

The first method of oxygen determination was published in 1922, by ter Meulen [33]. It applied a preliminary pyrolysis of analyzed compounds carried out in a quartz combustion tube (scheme 9).

$$S^*\ (C_xH_{2y}N_zO_m) \xrightarrow[\text{Temperature}]{} x\,(CO_2 + CO) + y\,H_2O + z\,NO_n$$

Scheme 9

Oxygen containing gas products of pyrolysis - CO_2 and CO, was subject to further reduction to water, determined gravimetrically (scheme 10).

$$x\,(CO_2 + CO) + y\,H_2O + z\,NO_n \xrightarrow[300\ ^{\circ}C]{H_2\,/\,Ni} m\,H_2O + z_{/2}\,N_2$$

Scheme 10

In the procedure published by Schutze, - organic substance is subject to a preliminary pyrolysis in an nitrogen atmosphere (void of oxygen) [72]. The pyrolysis products (CO_2 and CO) are passed over carbon glowing-hot to bright reddens, what causes full reduction of carbon dioxide to carbon monoxide (scheme 11).

$$x\,(CO_2 + CO) + y\,H_2O + z\,NO_n \xrightarrow[1000\ ^{\circ}C]{C\,/\,N_2} m\,CO + z_{/2}\,N_2$$

Scheme 11

The formed carbon oxide, treated with iodic anhydride, released stoichiometrically iodine (scheme 12), subsequently determined by the iodometric titration [132].

$$5\,CO \xrightarrow{I_2O_5} I_2 + 5\,CO_2$$

Scheme 12

Different modifications of this method function to today; the introduction of the physical methods to quantitative determination of carbon oxide formed (GC-IR, GC-TCD) permit considerable shortening of the method as well as its considerable automation [278,380,385,405,409,440].

During the past two centuries the elementary analysis passed a huge evolution. When as 150 years ago were the need, according from a qualitative composition, from 1 to 5 g of the analyzed substance [1-10], at present, applying the micromethods the quantity of milligram and even microgram range is sufficient [51,84,126,144,241,267,293,311,312,317,339,354,372,385,441,473].

The endeavour to economization of the analytical process, dictated with growth of demand on elementary analysis determination implied the research development over modification of earlier worked out procedures in direction of shortening of the time of analysis. Since most time consume gravimetric determinations of combustion products, it was tried to cut down these parts of an analytic process by the replacement of weighing of absorptive apparatuses by certain physical measurements, permissive on determination of CO_2, H_2O whether N_2, directly or indirectly in the combustion products. The elementary analysis, dominated by usage of the commercially accessible analyzers at present, pursuant the majority of analytic actions automatically, and so without the experimenter who stays only weighing substance's part [399,410], periodical tests of the apparatus, as well as an interpretation of the results. The exactitude of results increased also, so that the average error of microanalytical determinations does not exceed ± 0.2 %.

At the beginning of 1960., the elementary analysis becomes united with gas chromatography [196,202,209,229,232], what stimulated a dynamic development of constructed analyzers' automation, illustrated by the expanding scope of available analytical configurations, namely starting from the CH, through CHN, CHNO and/or CHNOS [183,256,273,281,282,284,299,304,305, 312-314,317,321,337,354,360]. In 1970., elementary analysis was conjuncted with computer processing methods [329,330,344]. An importance of this application increased successively in next decades [498].

The progress in the field of elementary analysis [151,177,186,192,339, 340,362,385,405,517,571] constitutes one of the most effective factors, influenced the present development of organic chemistry. The milligram or centigram range methods of elementary analysis pushed out the macro-chemical methods, making possible shortening of the time of analysis, more rational handling with the determined substances as well as chemical reagents, and also on the analyst's more convenient and more safe work.

Although introduction to the organic chemistry research a mass spectroscopy technique [297,407,464, 467,492,515,518,520,523,539,557,578] makes possible the settlement of the molecular formula of analyzed compound, and also the isotopic ratio of carbon and nitrogen atoms, the exact measurement of molecular ion mass does not replace the elementary analysis [557]. Induced, from second side, the utilization of the laser spectroscopy permits on a settlement of the C : H : N atoms ratios [568].

These techniques, however, do not deliver sufficient information, relating to a chemical purity of compounds analyzed. In contrary, the result of elementary analysis state both the purity degree of compound, as and the test of molecular mass. Therefore elementary analysis keeps fully its importance in organic chemistry.

2. Elementary Analysis of Carbon, Hydrogen and Nitrogen

Determination of carbon, hydrogen and nitrogen (CHN) belong to the most important signs of elementary analysis. The analytical procedures applied for these determinations underwent the evolution from Gay-Lussac, Dumas and Liebig era. This is reflected by their continuous development, across the determinations of carbon and hydrogen (CH) as well as the nitrogen (N), across simultaneous determinations of carbon, hydrogen and nitrogen (CHN) and since two decades the simultaneous determinations of carbon, hydrogen, nitrogen, sulfur and oxygen (CHNSO).

2.1. Determination of Carbon and Hydrogen

Beginning from the classic works of Gay - Lussac, Liebig and Pregl - the CH analysis applied the combustion the organic substance to carbon dioxide and water (scheme 1-3) and subsequent determination of these components. The *sine quanon* requirement of correct CH analysis was assurance of the quantitative course of both stages of the analytic procedure applied.

2.1.1. Combustion Process of Organic Compounds

The combustion of organic substance can be performed using one of the following variants:

a. the combustion using solid oxidant;

b. the combustion in an atmosphere of oxygen in the presence of a catalyst (Pt);
c. the combustion carried out by means of solid oxidant in the presence of oxygen;
d. the combustion in an atmosphere of oxygen at temperature 1000 °C.

Kainz and Horvatish [211,213,214] revealed that the oxidative activity of different solid oxidants applied for the combustion in the oxygenic atmosphere is different than exhibited in the anaerobic atmosphere. And so, in the atmosphere of oxygen the efficiency of oxygenation of representative oxidants changes in following order:

$Pd/O_2 > Co_3O_4 > MnO_2 > Pt/O_2 > Ni/O_2 > CuO > Cr_2O_3 > Fe_2O_3 > Mn_2O_3 > CeO_2 > ZnO > WO_3 > SiO_2$

The lowest temperature of oxidation activity of solid oxidants depends on a kind of oxide, and carries out 345 °C for Co_3O_4; 410 °C for MnO_2; and 445 °C for CuO [199].

The list of representative solid oxidants applied in the combustion analysis is given in Table 1. The comparison and profile of physico-chemical proprieties of various metal oxides applied in the elementary-combustion analysis (Cu, Co, Mn, Ni, Mg, Ag i Pb) was presented by Kirsten [239]. Kainz and Horvatish [199] as well as Vecera [315] introduced to the elementary analysis mixed catalysts ($CuO + Cr_2O_3$; $CuO + Co_3O_4$; CuO + Ag; Co3O4 + asbestos).

Table 1. Representative oxidants applied in combustion analysis.

No	**Oxidant**^{a,b}	**Products of combustion**^{b,c}	**Analy-sis**	**Literature**
1	$KClO_3$	$S^* + KClO_3 \rightarrow KCl + \mathbf{CO_2 + H_2O}$ $S^* + KClO_3 \rightarrow KCl + CO_2 + H_2O + \mathbf{NO_z}$	CH N	1 276
2	CuO	$S^* + CuO \rightarrow Cu_2O + \mathbf{CO_2 + H_2O}$ $S^* + CuO \rightarrow Cu_2O + CO_2 + H_2O + \mathbf{NO_z}$	CH N	2,28,43,185 179,277
3	$CuO + KClO_3$	$S^* + CuO + KClO_3 \rightarrow Cu_2O + KCl + CO_2 + H_2O + \mathbf{NO_z}$	N	276
4	$CuO + V_2O_5$	$S^* + 2\,CuO + V_2O_5 \rightarrow Cu_2O + V_2O_3 + \mathbf{CO_2 + H_2O}$ $S^* + 2\,CuO + V_2O_5 \rightarrow Cu_2O + V_2O_3 + CO_2 + H_2O + \mathbf{NO_z}$	CH N	20 13

5	$CuO +$ $CeO_2 +$ $PbCrO_4$	$S^* + CuO + CeO_2 + PbCrO_4 \rightarrow Cu_2O + Ce_2O_3 + PbO + Cr_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	70
6	$CuO +$ $M(OAc)_2$	$S^* + CuO + M(OAc)_2 \rightarrow M_2O + CO_2 + H_2O + \mathbf{NO_z}$	N	66
7	MnO_2	$S^* + MnO_2 \rightarrow MnO + \mathbf{CO_2} + \mathbf{H_2O}$ $S^* + MnO_2 \rightarrow MnO + CO_2 + H_2O + \mathbf{NO_z}$	CH N	28 35,65
8	$AgMnO_4$	$S^* + AgMnO_4 \rightarrow Ag_2O + Mn_2O_7 \rightarrow Ag_2O + MnO + \mathbf{CO_2} + \mathbf{H_2O} + NO_z$	CH	160-162,173, 175,326,343, 352
		$S^* + AgMnO_4 \rightarrow Ag_2O + Mn_2O_7 \rightarrow Ag_2O + MnO + CO_2 + H_2O + \mathbf{NO_z}$	N	99,100,107
		$S^* + AgMnO_4 \rightarrow Ag_2O + Mn_2O_7 \rightarrow Ag_2O + MnO + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	581
9	$MnO_2 +$ $SiO_2 +$ $K_2Cr_2O_7$	$S^* + K_2Cr_2O_7 + MnO_2 + SiO_2 \rightarrow MnSiO_3 + Cr_2O_3 + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	461
10	$MnO_2 +$ $Ag_2O +$ infusorial earth	$S^* + MnO_2 + Ag_2O \rightarrow MnO + Ag_2O + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	279,293
11	V_2O_5	$S^* + V_2O_5 \rightarrow V_2O_3 + \mathbf{CO_2} + \mathbf{H_2O} + NO_z$ $S^* + V_2O_5 \rightarrow V_2O_3 + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CH CHN	32,326,343,352 582
12	$AgVO_3$	$S^* + 2AgVO_3 \rightarrow Ag_2O + V_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	96
13	$CeO_2 +$ V_2O_5 / pumice	$S^* + CeO_2 + V_2O_5 \rightarrow Ce_2O_3 + V_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	96
14	$Ag_2Cr_2O_7$	$S^* + Ag_2Cr_2O_7 \rightarrow Ag_2O + Cr_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	96
15	$PbCrO_4$	$S^* + 2PbCrO_4 \rightarrow PbO + Cr_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	4
16	NiO	$S^* + NiO \rightarrow Ni + CO_2 + H_2O + \mathbf{NO_z}$ $S^* + NiO \rightarrow Ni + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	N CHN	107,123,151, 168 274

17	Co_3O_4	$S^* + Co_3O_4 \rightarrow CoO + \mathbf{CO_2} + \mathbf{H_2O}$	CH	23,96,184,185, 187,236,243, 245
		$S^* + Co_3O_4 \rightarrow CoO + CO_2 + H_2O + \mathbf{NO_z}$	N	169-172,194, 220, 264,397, 400,406,581
		$S^* + Co_3O_4 \rightarrow CoO + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	201,382
18	Co_3O_4 + Al + Fe_2O_3	$S^* + Co_3O_4 \rightarrow CoO + CO_2 + H_2O + \mathbf{NO_z}$ $2\ Al + Fe_2O_3 \rightarrow 2\ Fe + Al_2O_3$	N	429,580
19	Pt + O_2	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{H_2O}$	CH	17,167,214, 227, 308,237
		$S^* + O_2 \rightarrow CO_2 + H_2O + \mathbf{NO_z}$	N	356
		$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	582
20	O_2	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{H_2O}$	CH	22,53,108,113, 119,238
		$S^* + O_2 \rightarrow CO_2 + H_2O + \mathbf{NO_z}$	N	249,267,277
		$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	250,331
21	WO_3	$S^* + WO_3 \rightarrow W_2O_3 + \mathbf{CO_2} + \mathbf{H_2O}$	CH	206
		$S^* + WO_3 \rightarrow W_2O_3 + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	582
22	WO_3 + Ag_2SO_3	$S^* + WO_3 \rightarrow AgWO_2 + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	311
23	Ag_2WO_4 + Ag_2O	$S^* + Ag_2WO_4 + Ag_2O \rightarrow AgWO_2 + Ag_2O + \mathbf{CO_2} + \mathbf{H_2O} +$	CH	262
24	MnO_2 + WO_3 + SiO_2 + Cr_2O_3	$S^* + WO_3 + MnO_2 + SiO_2 + Cr_2O_3 \rightarrow MnSiO_3 + W_2O_3 + \mathbf{CO_2} + \mathbf{H_2O} + \mathbf{NO_z}$	CHN	386

[a] M – Cu or Hg; AcO – acetate. [b] **S*** - analyzed sample. [c] NO_z were subsequently reduced into N_2.

Particularly interesting methods were introduced by Marek and based on the combustion of substance in a quartz tube without solid oxidants [22], developed subsequently by Bennett [113], Belcher and Ingram [119], and others [385]. The oxygen balance occurring during combustion of organic samples containing carbon, hydrogen and oxygen was investigated by Rezl [448].

Utilization of gaseous oxygen to the combustion, involved the requirement of careful purification of the applied gas from any organic substances (passing over layers CuO, Co_3O_4 or Korbl catalyst [98]), and also its desiccation and decarbonization [385].

During the combustion of organic containing-nitrogen, sulfur, phosphorus and halogens substance the formed undesired products of these elements oxidation – has to be removed from the combustion products composition (by absorption on corresponding reactive filling of the tube). Thus, halogens and sulfur oxides are caught quantitatively on a silver gauze, situated in the terminal part of the combustion tube and warmed to temperature of 400-500 °C [71,79,118,156]. Another effective halogen and sulphur scavenger are Ag as well as Ag_2WO_4 (embedded on Chromosorb) [262] or Ag /Al_2O_3 [288].

Particularly large complications accompany the combustion of organic, fluorine-containing substances. This results from large durability of the C-F bond, and also from poor combustibility of this type of compounds. From other side, the products of combustion of fluorine-containing compounds react with quartz forming volatile silicon fluorides (SiF_4) and by this way shorten the time of use of the combustion tube; and also overstating carbon determination data (reaction with CO_2 absorbents) [125].

A removal of fluorine from combustion gases was achieved by application of MgO [148,149,174,275,280], Pb_3O_4 [181], CeO_2 [289], $AgVO_3$ [255,327], MnO_2 [244], or granulated NaF [203,346]. Pechanec for absorption of HF applied Ag_2CO_3 and $PbCO_3$ (500 °C) [257].

During the combustion of phosphorus-containing compounds one need the neutralization of phosphorus oxides during combustion formed. For this porpoise, according to Kasler, MgO is suitable perfectly [275]. Kozłowski and co. [342] determined the phosphorus oxides binding value exhibited by series of sorbents, in these, various metals and their oxides. These, in temperature of 750-900 °C were changed in the following order:

$MgO > Ag > AgMnO_4 > MnO_2 \sim Ni > Al_2O_3 > CeO_2 > CuO > Co_3O_4 > WO_3 > SiO_2$

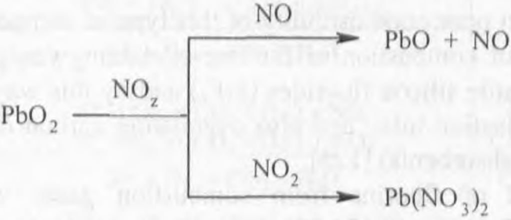
According to Binkowski and Gizinski [364,369,392], the ability to bond phosphorus oxides exhibited by various reagents (components of reactive fillings of the combustion tube) is in accordance with the following row:

$Ag\text{–}pumice > Ag\text{–}MnO_2 > MnO_2 > ZnO > Co_3O_4 > asbestos > pumice > Ag\text{–}Al_2O_3 > ZrO_2 > Al\text{–}Si > Al_2O_3 > MgO > CuO > CeO_2 > Si > WO_3$

On the ground of these investigations Giziński and Waśkowski worked out the composition of a reactive filling neutralizing effectively phosphorus oxides in products of combustion of different phosphorus-containing compounds [423].

The largest difficulties in the carbon determination appear in the case of analysis of nitrogen-containing compounds with regard to the formation of nitrogen oxides ($N \rightarrow NO_z$), overstating the carbon determinations. These nitrogen oxides can be removed from combustion gases, by the reduction or by chemical ligature with the help of suitable binding substances. Chronologically, the first used nitrogen oxides reducer was metallic copper, originally applied by Gay - Lussac [1,2] and Dumas [3], as and by other explorers [34,55,60,113,121, 139,172,210,263]. From other effective nitrogen oxides scavengers were applied: Ag [385], Ni [159], CeO_2 [86,89], MnO_2 [116,144,172,326,343], PbO [284] as well as very frequently PbO_2 [12,25,28,215,225-227].

Lead dioxide reacts with nitrogen oxides already at a temperature of 180-200 °C, binding it quantitatively in the form of lead (II) nitrate (scheme 13).



Scheme 13

It was found, that some substances, for instance hopcalites (hopcalite I: MnO_2–CuO–Co_2O_3–Ag_2O; hopcalite II: MnO_2–CuO) bind nitrogen oxides already at a room temperature. For their removal liquid absorbing solutions were also applied [385]. Detailed investigations on the nitrogen oxides absorption by application of a large number of various substances were undertaken by Kainz and Zidek [268].

The composition of representative reactive fillings of combustion analysis for the analysis of carbon and hydrogen (CH), nitrogen (N), and carbon, hydrogen and nitrogen (CHN), is presented in Table 2.

Table 2. Representative reactive fillings applied in elementary analysis.

No	Analysis	Combustion conditions	Combustion tube reactive fillings	Literature /Analyzer
1	CH	$S^{*b} + Ag_2WO_4{}^b + Ag_2O^b + O_2$ (1000 °C)	SiO_2-Ag_2O-Ag_2WO_4-MgO-Ag_2WO_4-Ag_2O-SiO_2 (800 °C)	254
2	CH	$S^* + Pt^b + O_2{}^e$ (1050 °C)	Pt-Cu-Ag (860-880 °C); Cu (500 °C)	308
3	CH (NPSOX)	$S^* + SiO_2{}^b + O_2{}^d$	Pt-CuO-Ag (700 °C); PbO_2–Ag (190 °C)	167
4	CH	$S^* + Al^a + V_2O_5 + O_2{}^e$ $(AgMnO_4)^f$ (800 °C)	SiO_2-Co_3O_4 + SiO_2-SiO_2 (800 °C); $AgMnO_4{}^f$ (500 °C)	326,343

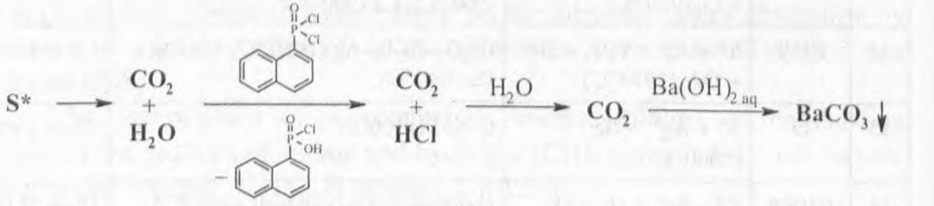
5	CH	$S^* + Sn^b + O_2$ (1000 °C)	Ag (500 °C); MnO_2 (20 °C)	242,260
6	N	$S^* + Pt^b + O_2$ (900 °C)	Co_3O_4 (750 °C); H_2/BTA (500 °C)	356
7	N	$S^* + CuO + CO_2$ (700 °C)	CuO-Cu (700 °C); CuO (200-300 °C)	385
8	N	$S^* + Pt^b + NiO + CO_2$ (1050 °C)	NiO-Ni (1000 °C); hopcalite (100-150 °C)	107,123,141
9	N	$S^* + Al^a$ (or Sn^a) CuO + O_2 (1050 °C)	SiO_2-CuO-Ag (950 °C); Ag-[CuO + SiO_2]-[Cu + SiO_2]-[CuO + SiO_2]-Ag (500 °C)	Heraus Rapid N
10	N	$S^* + Al^a + Co_3O_4$ (1050 °C)	Cu (800 °C)-CuO (550 °C)-Ag (250 °C)	397,581
11	CHN	$S^* + Al^b$ + He (1050 °C)	CuO (1050 °C); Cu (500 °C)	HP 185
12	CHN	$S^* + Ag^a + He + O_2^d$ (1050 °C)	CuO-Ag-MgO (850 °C); Cu (500 °C); SiO_2 (200 °C)	Technicon
13	CHN	$S^* + Ag^b + Co_3O_4 + He + O_2$ (900 °C)	Pt-Ag_2WO_4(MgO)-Ag_2O-Ag_2WO_4-Ag (900 °C); Cu (500 °C)	PE 240
14	CHN	$S^* + Al^a + V_2O_5 + He + O_2^c$ (1050 °C)	Cr_2O_3-Co_3O_4-Ag (1050 °C); Cu-CuO-Cu (640 °C)	CE m 1104
15	O	$S^* + Ag^a + He$ (1000 °C)	C-Ni-Pt (1000 °C)	CE m 1104
16	CHNS	$S^* + Sn^a + He + O_2^c$ (900 °C)	Oxido-reductive catalysts (900 °C)[g]	Flash 1112 EA
17	O	$S^* + Sn^a + He$ (1000 °C)	Ni-C (900 °C)	Flash 1112 EA
18	CHN	$S^* + Al^a + AgMnO_4^f + O_2 + He$ (800 °C)	Ag_2WO_4-ZrO_2-MnO (600 °C)	455
19	CHN	$S^* + Al^a + AgMnO_4^f + Cr_2O_3 + He$ (800 °C)	Pt-CuO-Co_3O_4-CuO (600 °C)	393
20	N	$S^* + H_2SO_4 + H_2CrO_4$ (20-200 °C)	CuO-Ag (500 °C)	381,421,422, 443,444

[a] Metallic capsule. [b] Boat. [c] Injection of a determined oxygen amount. [d] Air. [e] Oxygen (3%) in a helium carrier gas. [f] Product of decomposition in 500 °C. [f] As result of metallic capsule combustion (Sn) the temperature locally increased to 1800 °C.

The investigations over suppression of nitrogen oxides formation accompanied by catalytic combustions of nitrogen-containing compounds, were conducted by Pechanec [290,291,302,303].

Obtained ultimate combustion products, namely water and carbon dioxide - were determined subsequently; gravimetrically using a selective chemisorption/absorption (CO_2 on lime-soda and/or ascarite) and/or water ($CaSO_4$, $Mg(ClO_4)_2$, $CoCl_2$), and also gasometrically and/or volumetrically [385]. Presently, in an endeavor to automation of analytic process, frequently are applied electrochemical methods, in this coulometric and conductometric methods, also the thermal conductometric (TCD) and infra-red based detection (IRD) [385, Table 8] methods.

A representative example of the volumetric micro-method of hydrogen determination presents the method elaborated by Lindner [32,38,49,50,64]. This method is based on the reaction of hydrolysis of not volatile 1-napthyl-dichlorophosphine oxide, generating hydrogen chloride. The passage of the combustion gases by series-connected washers filled with water (absorption of HCl) and baryta water (absorption of CO_2), permits volumetric determination of both components (scheme 14).



Scheme 14

Numerous examples of the volumetric determinations of carbon and hydrogen were discussed in the review work of Bobrański [385].

The exact results were possible to get by applying the conductometric method of Cain [29], basing on a decrease of electrochemical conductivity of absorption solution occurring in result of the absorption of carbon dioxide, involving the reaction course:

$$2\ HO^- + CO_2 \rightarrow CO_3^{2-} + H_2O$$

Scheme 15

The conductometric method was successfully applied in several works [194,197,198,200, 228,240,251,258,310]. Accurate results of carbon dioxide determination were obtained also applying the coulometric-alkacimetric [233,310,324,332,351] or potentiometric [435] titrations. The water content was determined, by utilization of a Keidel hygrometer [189,207,235] or the reagent of Fischer (K-F reagent) [61].

$$H_2O + I_2 + SO_2 + 3\,Py \rightarrow 2\,Py \times HI + Py \times SO_3$$

Scheme 16

The reaction of water with the K-F reagent runs with a stoichiometric consumption of iodine, in accordance with the presented equation (scheme 16) [73]. The subsequent water determination can be performed on the way of coulometric regeneration (oxidation) of consumed in the reaction iodine (scheme 17) [190].

$$2I^- \rightarrow I_2 + 2e$$

Scheme 17

Quick determination of CO_2 is possible by application of infra-red absorbance based detectors (IRD) [216,269,337,385] as well thermal conductometric detectors (TCD) [222,240,280,385,388,419, Table 8].

The apparatus of Libieg-Pregl for determinations of carbon and hydrogen, underwent constant modifications directed on a growth of precision of signs, a decrease of the mass of analyzed sample as well as shortening of the time of analysis and its simplification, which was possible to reach by continuous development of automation. The representative CH analyzers, applied in the period preceding appearance of trade automatic analyzers, in this number: the analyzers of Bobrański [167], Gustin and Hofman [254], the apparatus of Binkowski [308] as well as Kozłowski [326,352], reflect the increasing level of automation.

The principle of working of apparatus for carbon and hydrogen determination (CH) according to Binkowski, the representative for its period, is presented in Fig. 3.

Analysis according to Binkowski:

An analyzed sample (3 mg) is placed in the boat 1 into the combustion tube 2 of the apparatus (Fig. 3), and burns up in an air stream, carefully cleaned by a prior passage through the purifying gas system 9-13. This consists of the dryer 9, the oxidation tube 10 and its furnace 11, and the absorbers 12 (ascarite) and 13 (anhydrone). The products of combustion (in majority consisted of CO, CO_2, NO_z and H_2O in a mixture with air) are transferred in the air stream through CuO and Ag layers (warmed to temp. 800-880 °C), then through a copper layer (warmed to temperature 500 °C) and subjected to further specific absorption: the water in the absorber 7 (filled with anhydrone) and the carbon dioxide in the absorber 6 (filled with ascarite), respectively. The content of carbon and hydrogen in the combusted sample was counted on the basis of mass increases of the corresponding absorbers (6 and/or 7).

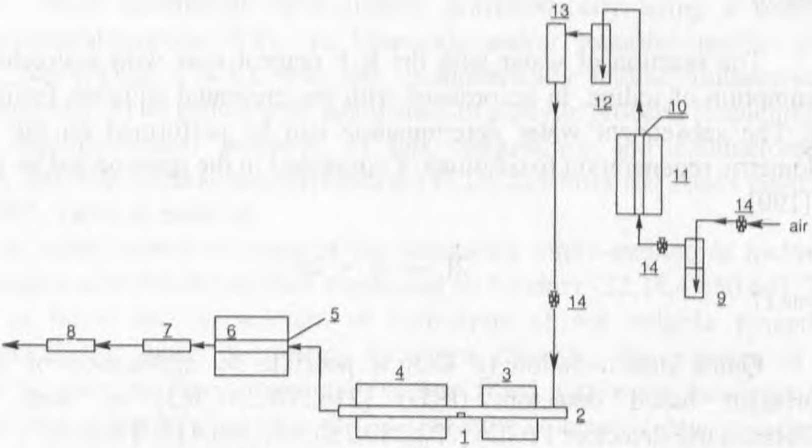
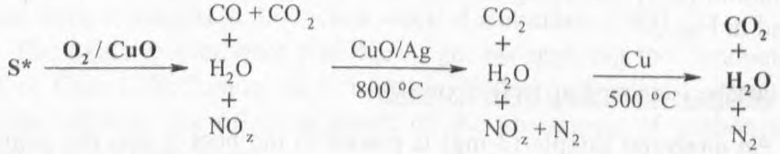


Fig. 3. Scheme of working of the apparatus for determination of carbon and hydrogen on milligram scale, according to Binkowski [308]:
1 – porcelain boat; 2 – combustion tube; 3 – electric movable furnace (1050-1070 °C); 4 – electric furnace (860-880 °C); 5 – reduction tube (Cu); 6 – reduction tube electric furnace (500 °C); 7 – water absorption pipe (anhydrone); 8 – carbon dioxide absorption pipe (ascarite); 9-13 – cleaning system for applied air [9 – dryer (conc. H_2SO_4), 10 – oxidation tube for air (CuO), 11 – electric furnace (800 °C), 12 – absorber (anhydrone), 13 – absorber (ascarite)]; 14 – valves.

Chemical transformations, occurring during this combustion analysis, are illustrated in scheme 18.



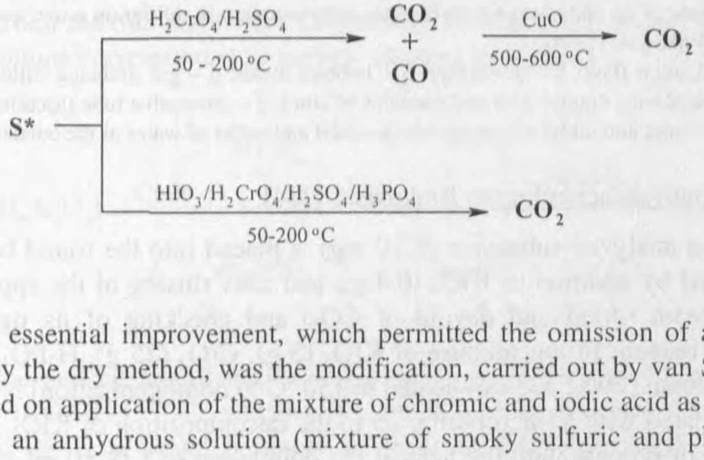
$$S^* \xrightarrow{O_2/CuO} \begin{matrix} CO + CO_2 \\ + \\ H_2O \\ + \\ NO_z \end{matrix} \xrightarrow[800\,^{\circ}C]{CuO/Ag} \begin{matrix} CO_2 \\ + \\ H_2O \\ + \\ NO_z + N_2 \end{matrix} \xrightarrow[500\,^{\circ}C]{Cu} \begin{matrix} \mathbf{CO_2} \\ + \\ \mathbf{H_2O} \\ + \\ N_2 \end{matrix}$$

Scheme 18

2.1.2. Carbon Determination by Wet Combustion Method

Despite advantages of a dry combustion method, the combustion of some organic substances are accompanied by serious difficulties. Examples of these are explosives, exacting of a special conduct application. Also, the combustion of samples bearing alkaline and alkaline-earth elements, requires the complicating the analytic procedure modifications. Moreover the combustion of organometallics including As, Sb, Bi, B or Ta, causes a durable damage of the tube or deactivation of the tube reactive fillings. In such cases, the carbon determination by the combustion carried out in a solution, so called "wet" combustion, introduced to elementary analysis by Messiner [15] presents a more profitable option.

Messinger oxidized by heating organic substance in a mixture of sulfuric and chromic acids. The carbon monoxide forming as a result of the reaction (scheme 19), is oxidized further to dioxide by a passage through the tube containing a glowing-hot copper oxide. The method of Messinger, being the conjunction of technique of combustion on wet (in solution in H_2SO_4) and on dry (in gas phase), in the original version of procedure [15], or in its modifications [16,42,44,48,54, 56,68], required therefore a rather enough complicated apparatus.



Scheme 19

An essential improvement, which permitted the omission of additional oxidation by the dry method, was the modification, carried out by van Slyke and Folch, based on application of the mixture of chromic and iodic acid as oxidative reagents in an anhydrous solution (mixture of smoky sulfuric and phosphoric acids). This reagent permits quantitative combustions of the organic carbon to carbon dioxide, without need of additional oxidation ($CO \rightarrow CO_2$) carried out in earlier versions in gas phase, in order to full conversion to dioxide. The formed carbon dioxide was determined subsequently manometrically [37,104], gravimetrically [91,109] or alkacimetrically [115].

Wide usage of Van Slyke's method disclosed its numerous limitations. Thus, the analysis of substance containing a high carbon contents (anthracene, camphor) usually leads to understated results of carbon content with errors exceeding 1%. Method is not suitable either to analysis of compounds insoluble in the Van Slyke's reagent, and also for volatile and/or subjected degradations to volatile derivatives compounds (compounds including N-methyl group, aryl halides, organophosphorus compounds) [385]. In the modification introduced by Binkowski [234], the method was adapted to determinations in the milligram scale, expanding also a range of its applicability. Ideological scheme of the apparatus applied by Binkowski for carbon determination by the wet combustion method, is presented in Fig. 4.

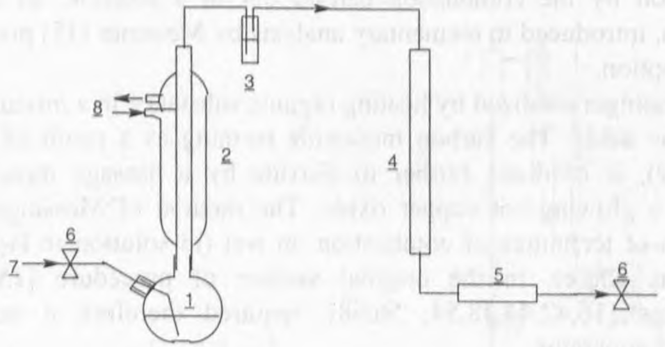


Fig. 4. Scheme of an apparatus for carbon wet determination in milligram scale, according to the method of Binkowski [234]:
1 – mineralization flask; 2 – condenser; 3 – bubbles-meter; 4 – gas drainage (filled with layers: asbestos, anhydrone, copper wire and particles of zinc); 5 – absorptive tube (ascarite); 6 – cutting off bolts; 7 – inlet and outlet of cleaned air; 8 – inlet and outlet of water of the condenser.

Analysis according to Binkowski [234]:

An analyzed substance (3-10 mg) is placed into the round bottom flask 1, followed by addition of KIO_3 (0.4 g), and after rinsing of the apparatus with an air stream (dried and devoid of CO_2) and checking of its tightness, the oxidative reagent [5 ml; mixture of KIO_3 (5 g), CrO_3 (25 g), H_3PO_4 (85%; 167 ml) and oleum (20%; 333 ml) heated in 150 °C to homogenization] is added. The flask is heated with a microburner up to the decomposition of KIO_3, controlling the speed of process with the help of the bubble-meter 3 (8-10 ml / min). After combustion of the substance (about 20 min), the apparatus is rinsed with a stream of air, (20 ml/min), in order to washout the whole quantity of produced CO_2 (20 min). The formed gas mixture is passed through the drying pipe 5 (removal of water vapor and volatile acids) and then through the absorptive pipe 6, where the quantitative absorption of CO_2, subsequently determined gravimetrically, occurs. The carbon content was counted on the ground of the increase of mass of the absorber 6, after deduction of the background (0.1 to 0.15 mg). The time of analysis: ca. 40 min.

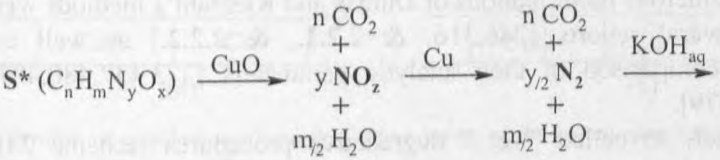
Other, present methods of analysis of the carbon content in organic substances, as and in environmental samples (OC, TC, TOC, TIC) using the wet-combustion method of mineralization (in solution), are discussed in the chapter 4.1.

2.2. Determination of Nitrogen

Determination of nitrogen in nitrogen-containing organic compounds can be achieved after preliminary degradation (mineralization) to simple nitrogenous inorganic compounds, in these ammonia, molecular nitrogen, nitrogen oxides (NO or NO_2) or to ions of nitric acid (NO_2^- and / or NO_3^-).

The degradation was usually carried out according to three fundamental methods: the method of Dumas, the method of Kjeldahl as well as the method of catalytic hydrogenation.

In the classic method of Dumas, the organic substance is mixed with copper oxide (CuO) and it burned in the combustion tube in a carbon dioxide atmosphere [3]. The formed combustion products (CO_2, H_2O and NO_z) are passed through a glowing-hot copper layer; where nitrogen oxides are reduced into molecular nitrogen, and the obtained mixture of transformed products of the combustion (CO_2, H_2O and N_2) is directed to the azotometer. Here in a solution of KOH, carbon dioxide underwent quantitative absorption, and due to this, the measured volume corresponded to formed nitrogen (scheme 20).

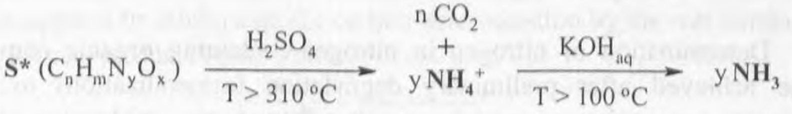


$$S^*(C_nH_mN_yO_x) \xrightarrow{CuO} \begin{array}{c} n\,CO_2 \\ + \\ y\,NO_z \\ + \\ {}^{m}\!/_{2}\,H_2O \end{array} \xrightarrow{Cu} \begin{array}{c} n\,CO_2 \\ + \\ {}^{y}\!/_{2}\,N_2 \\ + \\ {}^{m}\!/_{2}\,H_2O \end{array} \xrightarrow{KOH_{aq}} {}^{y}\!/_{2}\,N_2$$

Scheme 20

In the present modifications of Dumas method, the formed products of combustion (CO_2, H_2O, NO_z whether N_2) are subject to an automatic analysis. During this, the combustion products are separated chromatographically with subsequent post-column instrumental determination, using usually thermal conductometric detectors [TCD] (CO_2, H_2O, N_2) [385,572, Table 8] and/or infra-red detectors [IRD] (CO_2, H_2O) [385,572, Table 8], and/or chemiluminiscence detectors [CLD] (NO_z) [436,440, 483,484,489,502].

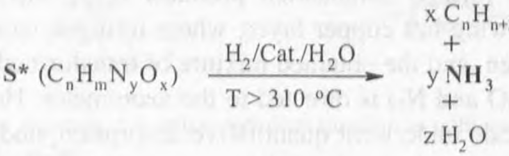
In Kjeldahl's method [13], the organic substance is mineralized by warming in a solution of concentrated sulfuric acid, during which the "organic" nitrogen (TON - *total organic nitrogen*; TBN - *total bound nitrogen*) converts into ammonium sulfate. The formed solution is alkalized, and released ammonia is determined in a separate flask, most often by means of the alkacimetric titration (scheme 21).



$$S^* (C_nH_mN_yO_x) \xrightarrow[T > 310\,^\circ C]{H_2SO_4} \begin{matrix} n\,CO_2 \\ + \\ y\,NH_4^+ \end{matrix} \xrightarrow[T > 100\,^\circ C]{KOH_{aq}} y\,NH_3$$

Scheme 21

In the method of catalytic hydrogenation, the organic substance was heated in a stream of hydrogen in the presence of suitable metallic catalysts, causing the reduction of organic nitrogen (nitrogen bounded) to ammonia [80,120], determined further by titration (scheme 22).

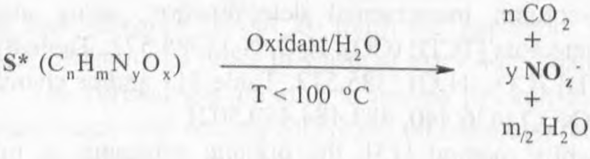


$$S^* (C_nH_mN_yO_x) \xrightarrow[T > 310\,^\circ C]{H_2/Cat./H_2O} \begin{matrix} x\,C_nH_{n+2} \\ + \\ y\,NH_3 \\ + \\ z\,H_2O \end{matrix}$$

Scheme 22

The numerous modifications of Dumas and Kjeldahl's methods were the subject of several reports [246,316, **& 2.2.1.**, **& 2.2.2.**] as well as the experimental comparison of their analytic parameters [373,437,480,487,507, 526,566,577,579].

In other, so called "wet " degradative procedures (scheme 23), the mineralization of nitrogenous compounds were carried out on the way of UV-photo-oxidation (UV/ $K_2S_2O_8/H_2O$) [484, Table 11], dichromate oxidation ($H_2SO_4/K_2Cr_2O_7$) [516, Table 11], or with microwaves-induced mineralization [434,437,456,466,528,529, Table 11].



$$S^* (C_nH_mN_yO_x) \xrightarrow[T < 100\,^\circ C]{Oxidant/H_2O} \begin{matrix} n\,CO_2 \\ + \\ y\,NO_z^- \\ + \\ {}^m/_2\,H_2O \end{matrix}$$

Scheme 23

Created as a result of the oxidative degradation (photo-oxidation or microwave-promoted oxidation) of organic substance - the ions of nitric (III and/or V) acids, were determined spectro-photometrically [494,501,555] or electrochemically [526].

An interesting method of the nitrogen determination by the "wet" oxidative degradation, followed by subsequent reduction of nitrogen oxides formed to molecular nitrogen, and its final TCD determination was presented by Ventura [381,421,443,444].

Several methods of nitrogen determination applied radiochemical procedures [286,370,371,436,475,539,561,567], mass spectroscopy [407,464, 523,578] or other physico-chemical methods [479,538,574].

2.2.1. Determination of Nitrogen by the Method of Dumas

The first, milligram scale method of nitrogen determination, based on Dumas procedure, came into being thanks to Pregl works [25]. And here, similarly as in the case of the CH determination, a decrease of the substance analyzed quantity disclosed many imperfections of Dumas apparatus.

The investigations carried out by Pregl exhibited, that copper used for the reduction of nitrogen oxides, at a temperature 650 °C reduced also carbon dioxide to monoxide - unsolvable in an solution absorbing of the azotometer, and therethrough elevating the results of nitrogen determination. To prevent this, Pregl introduced to Dumas combustion tube a third layer, folded from copper oxide, the task of which was the conversion of carbon oxide to dioxide (Fig. 5).

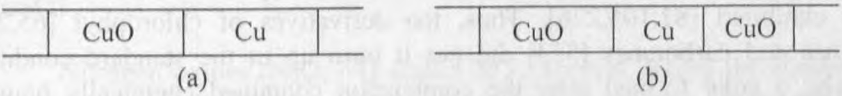
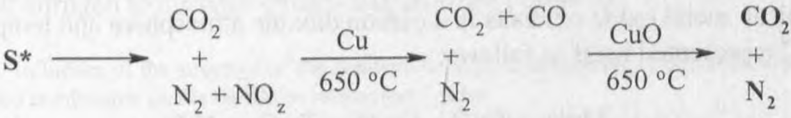


Fig. 5. Profile of distribution of reactive filling layers of the combustion tube: (a) according to Dumas, (b) - in Pregl's modification

These processes setting in the combustion tube by Pregl, occurred in accordance with scheme 24.



$$S^* \longrightarrow \begin{matrix} CO_2 \\ + \\ N_2 + NO_z \end{matrix} \xrightarrow[650\,^\circ C]{Cu} \begin{matrix} CO_2 + CO \\ + \\ N_2 \end{matrix} \xrightarrow[650\,^\circ C]{CuO} \begin{matrix} CO_2 \\ + \\ N_2 \end{matrix}$$

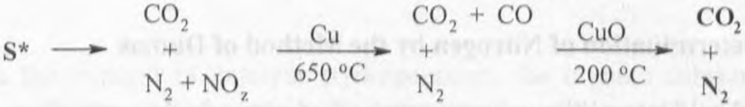
Scheme 24

Halla [45] revealed, that the location of the additional layer of CuO leads to extortionate results of the nitrogen, resulting from the reaction of dissociation of copper oxide, setting in temperature of 650 °C (scheme 25).

$$2\,CuO \xrightarrow[650\,^\circ C]{} Cu_2O + 0.5\,O_2$$

Scheme 25

Due to this, Fisher [78] recommended heating of the terminal layer with CuO only to 200 °C temperature, in which the oxidation of carbon oxide to dioxide ($CO \rightarrow CO_2$) was quantitative whereas the dissociation of copper oxide ($2CuO \rightarrow Cu_2O + 0.5O_2$) did not run (scheme 26).



$$S^* \longrightarrow \begin{matrix} CO_2 \\ + \\ N_2 + NO_z \end{matrix} \xrightarrow[650\,^{\circ}C]{Cu} \begin{matrix} CO_2 + CO \\ + \\ N_2 \end{matrix} \xrightarrow[200\,^{\circ}C]{CuO} \begin{matrix} CO_2 \\ + \\ N_2 \end{matrix}$$

Scheme 26

Hozumi and Amako [188] conducted the investigation over the relationship between the temperature of the reduction layer and its thickness. Other sources of overstating the results of nitrogen determination resulted from porosity of applied oxidants and/or sorbents, as a result of which, air contained in them was washed out to a carrier gas during the analysis. Elimination of these factors works of Flaschentrager [41] and other explorers [39,46,52,53] were consecrated.

In time, other limitations of Dumas method, depending mainly on understating of the nitrogen content results in heterocyclic aromatic compounds, were exhibited [81,105,276]. Thus, the derivatives of chlorophyl [65,262], pterynes and carboranes [323] did not it burn up in the standard conditions entirely; a coke formed after the combustion contained chemically bounded nitrogen. However, in the case of long chain aliphatic compounds, methane during the combustion was formed, overstating the azotometer indication [107,123,124,133]. In the case of analysis of this type of compounds, the substance analyzed was mixed with composites of CuO and $KClO_3$ [276], or CuO and V_2O_5 [20], or CuO and the salts of copper or mercury [66].

In investigations of Kainz [213], the oxygenation effectiveness exhibited by typical metal oxide oxidants in a carbon dioxide atmosphere and temperature 650 °C represented itself as follows:

$$MnO_2 > CuO \sim Co_3O_4 > Fe_2O_3 > NiO$$

Mitsui [152] investigated the thermochemical equilibria established between Cu_2O, CuO and CO_2, at a temperature 750-800 °C, affirming the course of following reactions (scheme 27).

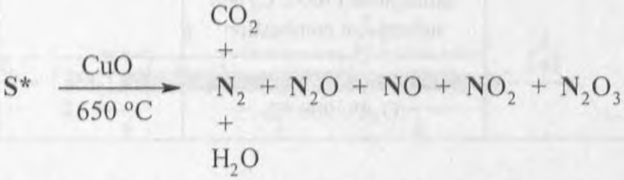
In connection with above mentioned, Mitsui the usage of a copper layer, heated to 550 °C, as the terminal layer recommended. Fischer [78] heated the final part of the combustion tube, containing CuO, to 200 °C, in which carbon oxide underwent a quantitative oxidation ($CO \rightarrow CO_2$) whereas copper oxide did not undergo a thermal dissociation ($CuO \rightarrow Cu_2O + O$).

$$2\,CuO \xrightarrow[750\text{-}800\,^{\circ}C]{CO_2} Cu_2O + 0.5\,O_2$$

$$2\,Cu + CO_2 \xrightarrow[750\text{-}800\,^{\circ}C]{CO_2} Cu_2O + CO$$

Scheme 27

During the combustion process, organic nitrogen is converted to a mixture of nitrogen and oxides of nitrogen exhibiting different degrees of oxidation ($N_2 + N_2O + NO + NO_2 + N_2O_5$) (scheme 28).



$$S^* \xrightarrow[650\,^{\circ}C]{CuO} \overset{\overset{CO_2}{+}}{N_2} + N_2O + NO + NO_2 + N_2O_3 \quad \underset{\underset{H_2O}{+}}{}$$

Scheme 28

Nitrogen oxides (N_2O, NO and/or NO_2) formed during the combustion, exhibit different solubility in alkaline solutions, they contain in the particle of oxide also different number of nitrogen atoms (N_2O *vs* NO_2). Therefore, the prior reduction of nitrogen oxides to molecular nitrogen, carried out before entrance of the combustion gases to the azotometer, is necessary.

A considerable influence of the structure as well as the way of combustion of nitrogen-containing compounds on the conversion degree of organic nitrogen to nitrogen oxides was affirmed (Table 3).

Table 3. Influence of the structure of the combusted nitrogen-containing compounds and the type of applied combustion on the formation of nitrogen oxides.

No	Class of analyzed compounds	Combustion	Degree of conversion [%] N → NO_x	Literature
1	Amines	Thermal decomposition	26%	62
		Combustion in a stream of oxygen	1-17%	106
2	Nitriles	Thermal decomposition	59%	62

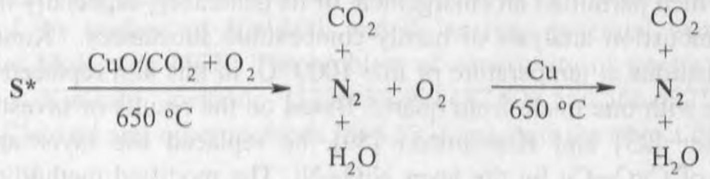
3	Nitro compounds	Thermal decomposition	59%	62
		Combustion in a stream of oxygen	82-97%	106
4	Heterocyclic compounds	Thermal decomposition	59%	62
		Combustion in a stream of oxygen	7-40%	106
5	Aromatic nitro compounds	Ignition combustion (O_2/Pt; 900 °C)	Up to 13%	287
6	Various nitrogen-containing compounds	Combustion in empty tube (O_2/Pt; 900 °C)	-	108
		Pyrolysis in nitrogen atmosphere (1000 °C) and subsequent combustion	-	292
		Combustion in empty tube (O_2/Pt; 900 °C)	1-8%	291

Czumaszenko [223] subjected the substance analyzed to the preliminary pyrolysis; in result of which, the majority of organic nitrogen was converted into molecular nitrogen (reductive action of organic carbon).

The temperature of CuO layer exerted a large influence on the exactitude of measurements. Thus, usually higher than 650 °C [385], in several works in range 700-800 °C [262], and for hardly combustible compounds and/or giving underestimated results at least 1000 °C [99,114,138].

One of the complete combustion substance (hardly-combustible compounds) affirmer ways, consists the combustion in an carbon dioxide including, the admixture of oxygen, atmosphere [69,99,127,129,131,136,154, 170,249,267,275,277,351]. For absorption of an oxygen excess, the reactive filling, equipped with situated in the end of the combustion tube copper layer (metallic or on mineral carrier), is applied [232].

The apparatus to the volumetric determinations of nitrogen according to Dumas method, based on described procedure (chemical reactions occurring during the procedure are presented on scheme 29) is illustrated in Fig. 6.



$$S^* \xrightarrow[650\ ^{\circ}C]{CuO/CO_2 + O_2} \begin{matrix} CO_2 \\ + \\ N_2 \\ + \\ H_2O \end{matrix} + O_2 \xrightarrow[650\ ^{\circ}C]{Cu} \begin{matrix} CO_2 \\ + \\ N_2 \\ + \\ H_2O \end{matrix}$$

Scheme 29

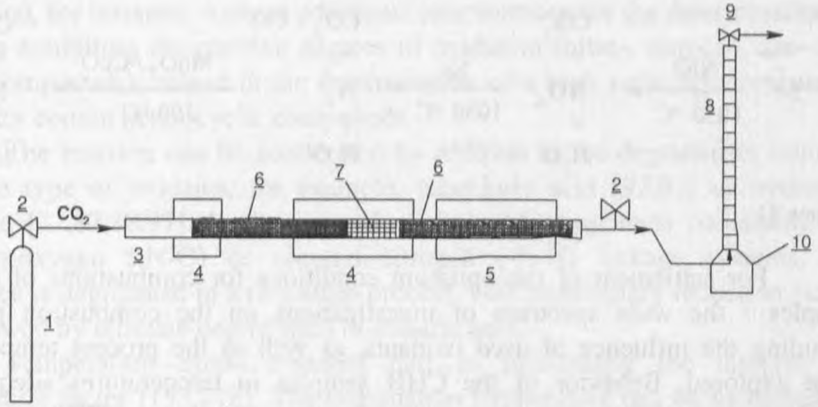
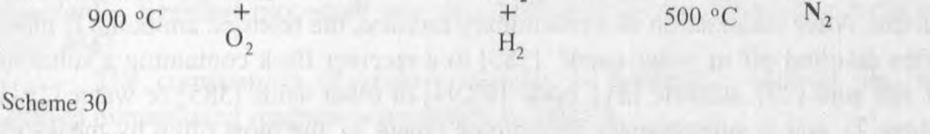


Fig. 6. Scheme of apparatus for Dumas nitrogen determination:
1 – carbon dioxide bottle; 2 – needle valve; 3 – combustion tube; 4 – electric furnace (700 °C); 5 – electric furnace (200-300 °C); 6 – layer of CuO; 7 – copper gauze; 8 – layer of CuO; 9 – azotometer; 10 – connection with reservoir of KOH solution.

In the method elaborated by Trutnowski [356], the sample is burnt out in oxygen, the formed nitrogen oxides along with an oxygen excess are reduced by means of hydrogen, which excess in turn is removed on a copper oxide layer (scheme 30).

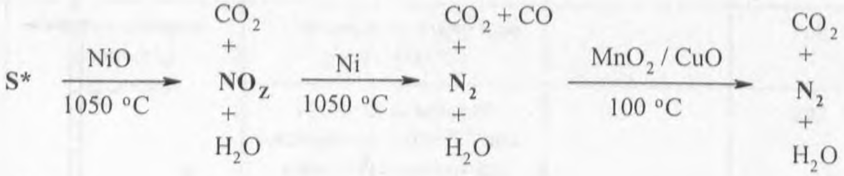


$$S^* \xrightarrow[900\ ^{\circ}C]{O_2 / Pt} \begin{matrix} CO_2 + H_2O \\ + \\ NO_z \\ + \\ O_2 \end{matrix} \xrightarrow{H_2} \begin{matrix} CO_2 + H_2O \\ + \\ N_2 \\ + \\ H_2 \end{matrix} \xrightarrow[500\ ^{\circ}C]{CuO} \begin{matrix} CO_2 + H_2O \\ + \\ N_2 \end{matrix}$$

Scheme 30

According to Kirsten [151], this course of action leads to extortionate results of nitrogen determination. This statement is in opposition to works of Mauser and Egli [155], as well as other explorers [385].

Kirsten [107,123,141] introduced a modification to the method of Dumas, which permitted an enlargement of its generality, especially in reference to the combustion analysis of hardly-combustible substances. Kirsten carried out combustions at temperature of line 1000 °C; in this aim replaced traditional glass tube with one made from quartz. Based on the results of investigations of Kurtenacker [23] and Kapustinski [59], he replaced the layer arrangement consisted of CuO–Cu by the layer NiO–Ni. The modified method of Kirsten-Dumas (scheme 31) was also adapted to the milligram scale [179].



$$S^* \xrightarrow[1050\ ^\circ C]{NiO} \begin{matrix} CO_2 \\ + \\ NO_z \\ + \\ H_2O \end{matrix} \xrightarrow[1050\ ^\circ C]{Ni} \begin{matrix} CO_2 + CO \\ + \\ N_2 \\ + \\ H_2O \end{matrix} \xrightarrow[100\ ^\circ C]{MnO_2 / CuO} \begin{matrix} CO_2 \\ + \\ N_2 \\ + \\ H_2O \end{matrix}$$

Scheme 31

For settlement of the optimum conditions for combustions of organic samples - the wide spectrum of investigations on the combustion process, including the influence of used oxidants, as well as the process temperature, were explored. Behavior of the CHN samples in temperatures adequate to combustion conditions was also studied by the utilization of TGA as well as termogravimetrical methods [425].

2.2.2. Nitrogen Determination by the Method of Kjeldahl

The method of Dumas, though presents the most general method of nitrogen determination, is not useful for the samples occurring in a form of aqueous solutions (in urine, blood, tissue homogenizates, physiological liquids, etc.). In such cases more profitable is the method of Kjeldahl, as quicker and using less complicated apparatus.

Kjeldahl's method is based on the degradation of organic nitrogen-containing compounds (mineralization) in concentrated sulfuric acid (stage 1), in result of which the bounded nitrogen converts by the reduction to ammonium sulfate. After alkalization of a reactionary mixture, the released ammonia is most often distilled off in water vapor [385] to a receiver flask containing a solution of salt acid [25], sulfuric [31], boric [90,94] or other acids [385] or water [191] (stage 2), and is subsequently determined (stage 3), the most often by means of the alkacimetric titration.

The method of Kjeldahl presenting in the classical elaboration (1883) the limited use, as result of subsequent improvements became one of more practical analytic methods [13,573,576]. The details relating the various modifications of the method of Kjeldahl were described by Bradstreet [246]. The evolution of the method of Kjeldahl, and its analytic potential was recently discussed by McKenzie [472]. The problem of superiority or compatibility of Dumas and Kjeldahl methods [373,437,480,487,507,526,566,577], or the method of Kjeldahl and other methods [296,573], presents the object of constant considerations.

According to present standards, the range of applicability of Kjeldahl's method, retreats still the enhanced versions of the method of Dumas. It can not be applied, for instance, without additional interventions for the determination of nitrogen exhibiting the positive degrees of oxidation (nitro-, nitrozo-, azo- and azoxy-compounds), or/and in the determination of a high volatility compounds or/and for certain heterocyclic compounds.

The reaction can be accelerated by addition to the degradation solution of some type of oxidants, for example, perchloric acid [92,93] or hydrogen peroxide [77,87,88,97]. In the case of analysis of compounds containing the nitrogen-oxygen (-N-O) or nitrogen-nitrogen (-N-N) linkage systems, the substance is degradated in a two-stage process, with preliminary reduction (stage I), followed by ultimate degradation in sulfuric acid.

Temperature exerts essential part as influencing the integrity of degradation factor [153,218]. The degradation temperature can be increased by the addition of K_2SO_4 (can not be replaced by Na_2SO_4 [178]) to 410 °C, and must not be lower than 380 °C [18,111,130].

Decompositions usually are completed after ca. 15 min; in case of derivatives of pyridine can last even up to 4 h [101]. The compounds containing nitrogen on the higher than -3 degree of oxidation (occurring in functions: $-NO_z$, -N-N-, -N=N-, etc.) do not undergo the quantitative degradation to ammonia (understated results of nitrogen). In these cases, the degradation solution was supplied by various additions, in these by phenols, salicylic or thiosalicylic acid, glucose, alone or as the combinations of these compounds (table 4). The most effective method turned out the two-stage procedure, in which, before the ultimate degradation in sulfuric acid, the preliminary reduction of nitrogenous functions by means of hydrogen iodide was applied [57,87,137,145,180]. Kjeldahl's digestion procedure was also facilitated by the microwave radiation [457,466].

The composition of various variants of Kjeldahl's method and the applied mineralizing reagents is presented in Table 4.

Table 4. Composition of various variants of Kjeldahl's method

No	**Kjeldahl's degradation**		**Reaction**	**Type of degradated compounds**	**Literature**
	I stage of degradation	**II stage of degradation**			
1	H_2SO_4		$N \rightarrow NH_3$	Amines, amides	13
2	$H_2SO_4 + CuSO_4$		$N \rightarrow NH_3$	Amines, amides	28,509
3	$H_2SO_4 + K_2SO_4$		$N \rightarrow NH_3$	Amines, amides	18,111,130,178
4	$H_2SO_4 + HClO_4$		$N \rightarrow NH_3$	Amines, amides	92,93
5	$H_2SO_4 + H_2O_2$		$N \rightarrow NH_3$	Amines, amides	77,87,88,97
6	$H_2SO_4 + Se$		$N \rightarrow NH_3$	Amines, amides	47,95,112,125
7	$H_2SO_4 + Se + Hg$		$N \rightarrow NH_3$	Amines, amides	67,85,102,117, 499
8	$H_2SO_4 + K_2SO_4 + Hg$		$N \rightarrow NH_3$	Amines, amides	24,122,128
9	$H_2SO_4 + Na_2S_2O_3$		$N \rightarrow NH_3$	Azides	147
10	H_2SO_4 + Ar-OH[a]		$N \rightarrow NH_3$	Amines, amides	14
11	H_2SO_4 + salicylic acid		$N \rightarrow NH_3$	Amines, amides	27,493
12	H_2SO_4 + thiosalicylic acid		$N \rightarrow NH_3$	Amines, amides, DNB	145,154
13	H_2SO_4 + glucose		$N \rightarrow NH_3$	Nitro compounds	40
14	HI	H_2SO_4	$N \rightarrow NH_3$	Nitro-, azo-, hydra-zine compounds	58,146
15	HI + P	$H_2SO_4 + K_2SO_4 + Se + HgSO_4$	$N \rightarrow NH_3$	Amides, nitro-, azo-, hydrazine compounds	385
16	$Zn + HCl_{aq}$ + AcOH	H_2SO_4	$N \rightarrow NH_3$	Nitro compounds	137
17	$Zn + HCl_{aq}$ + MeOH	H_2SO_4	$N \rightarrow NH_3$	Nitro compounds	180
18	$CrCl_2 + H_2SO_4 + H_2O$	$H_2SO_4 + K_2SO_4$	$N \rightarrow NH_3$	Nitro compounds	165

[a] Ar-OH = fenol, 1-naftol, 2-naftol, pirocatechine, pirogallol, fluoroglucine, galusic acid

A typical procedure of degradation of nitrogen-containing compounds into ammonia, according to modified by Bobrański the Kjeldahl's procedure is given below [385].

The digestion of organic substance not including the N–O and/ or N-N bonds:

A sample of substance (1-5 mg) was poured into Kjeldahl's flask, followed by the addition of sulfuric acid (1 ml), and the catalyst [0.15 g; received by dissolving K_2SO_4 (32 g), $HgSO_4$ (5 g) and selenium (1 g)]. The flask was heated to boil ca. 15 min. In case of incomplete digestion, hydrogen peroxide (ca. 0.1 ml, 30 %) was added, and the formed reaction solution was heated for additional 15 min.

The digestion of organic substance including the N-O and/or N-N bonds:

A sample of substance (1-5 mg) was poured into Kjeldahl's flask, followed by addition of hydroiodic acid (1 ml; d = 1.7 g / ml) and several grains of red phosphorus. The contents of the flask was heated to gentle boiling for 30 min, the sulfuric acid (1.6 ml) was then added and the flask was heated until water and hydrogen iodide evaporated. After 1.5 h (clear solution, the absence iodine in the flask) the catalyst (0.15 g) was added and the digestion solution was heated for another 30 min.

Subsequent nitrogen determination is carried out by titrations of formed ammonia. In order that, ammonia was usually released from ammonium sulfate by alkalization of the mother solution, followed by distillation off in a stream of water vapor [140,385]. The successive determination of ammonia was performed using alkacimetric [26,27,90,94, 100,191,316] or iodometric [19,30,126] titrations, coulometrically [351] or colorimetrically [477], or by means of the Nessler's reagent (scheme 32) [182,195] or with the help of the GD – FIA procedures [509].

$$NH_3 + HgI_2 \rightarrow Hg(NH_2)_2$$

Scheme 32

In the iodometric procedures applied for the ammonia determination, ammonia is absorbed in an aqueous solutions of potassium diiodate [$KH(IO_3)_2$] [30,126] or in an acidified solutions of potassium chlorate [31]. The released iodine, in quantities proportional to the concentration of hydrogen ions, is successively titrated by means of a sodium thiosulfate solutions (scheme 33).

$$5\,I^- + IO_3^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$

Scheme 33

In the row of works, ammonia was determined directly in the post-degradation mixture, with omission of the alkalization stage, the distillation off of ammonia and its sequent absorption [30,36,63,103,110,157,166,204,212]. One of these methods [36] is based on the exact neutralization of the digestion mixture, the subsequent addition of formalin and successive determination of sulfuric acid formed (scheme 34).

$$(NH_4)_2SO_4 + 6\,CH_2O \rightarrow (CH_2)_6N_4 + 2\,H_2SO_4 + 6\,H_2O$$

Scheme 34

In another procedure, ammonia was determined indirectly, after previous oxidation of ammonia by sodium hypobromite, and the successive iodometric determination of the excess of hypobromite applied [30,63,212] (scheme 35).

$$2\,(NH_4)_2SO_4 + 3\,NaOBr \rightarrow 3\,NaBr + 3\,H_2O + H_2SO_4 + N_2$$

$$NaOBr + 2\,KI + 2\,HCl \rightarrow 2\,KCl + NaBr + H_2O + I_2$$

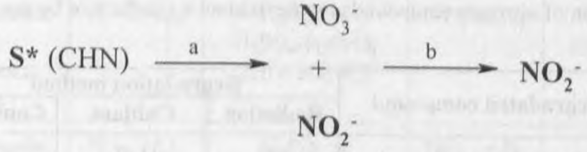
Scheme 35

In an alternative approach, the excess of hypobromite was determined by back-titration of the excess of hypobromite by means of the standardized solution of sodium arsenite [166,204] (scheme 35).

2.2.3. Determination of Nitrogen by Oxidative and Oxidative-Reductive Degradation Methods

An alternative to Kjeldahl method is the oxidative degradation of nitrogen-containing compounds, based on the "wet oxidation" of nitrogen to the nitrate ions. As oxidation reagents, usually atmospheric oxygen [528,529], hydrogen peroxide [252,298,367,411], potassium persulfate [453,469,471,484] or chromic acid [516], alone or in coupling with UV or microwave irradiation, were applied.

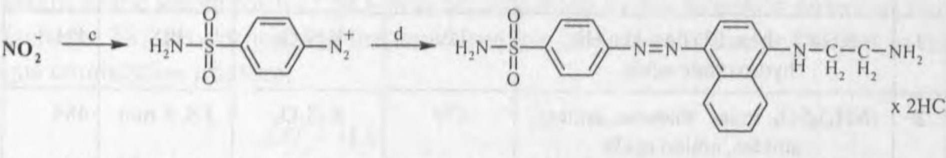
The oxidative degradation of nitrogen-containing compounds carried out in solutions occurs with the formation of nitrate ion, which undergoes further, partial reduction to nitrite ion [252,484]. The nitrite ion, can be determined directly or indirectly using the methods of molecular spectroscopy, under condition of the quantitative reduction of nitrate to nitrite ions. This conversion, is most often carried out by the reduction by means of activated cadmium [366,494], EDTA and/or DTPA [481], or hydrazine [497]. The principle of the conversion of nitrogen-containing compounds to nitrite ion is presented in scheme 36.



a – UV-induced oxidation (O_2, H_2O_2 or $K_2S_2O_8$); b – reduction of nitrate to nitrite ions (Cd, EDTA, or DTPA)

Scheme 36

The formed nitrite ions, were determined on the base of dye of Griess formation (scheme 37), and its subsequent spectrophotometrical determination [366,367,469,471494,497].



c – diazotization of sulfanilide; d – conjunction with 1-napthyletylenediamine (formation of Griess dye)

Scheme 37

The comparison of the two major methods of the "wet-mineralization" – the method of Kjeldahl and the UV-promoted photooxidation was the object of a row of comparative works, in this Henriksen's [298], Gustafsson's [411], Kroon's [469] and McKelvie's [479], which exhibited the comparable results for majority of all compounds investigated.

The UV-promoted photooxidation method led to worse results in the case of degradation of hydrazines and diazo-compounds (60% in relation to results obtained by HTC methods), and comparable {90-95% in [449] and > 95% in [471]} in the case of degradations of other nitrogen-containing compounds.

The representative papers on the oxidative degradation of nitrogen-containing compounds, by radiation induced methods (CHN → NO_2^-), are listed in Table 5.

The methods based on wet-oxidative degradation of nitrogen-containing compounds, followed by the subsequent reduction of formed nitrogen oxides to molecular nitrogen, are presented in Table 6.

Table 5. Degradation of nitrogen compounds by the oxidative – inductive by the radiation methods ($CHN \rightarrow NO_z^-$)

No	Type of degradated compound	Degradation method[a]			Literat.
		Radiation	Oxidant	Conditions	
1	NH_4Cl, thiourea, heterocyclic amines	UV	H_2O_2	2-3h	252
2	NH_4Cl, KNO_3, heterocyclic amines	UV	H_2O_2	4h	298
3	Several nitrogen (and/or phosphorus) containing compounds	UV	H_2O_2	3h	367
4	Amines, amides, amino acids, proteins	UV	H_2O_2	1-3h	411
5	$NaNO_2$, $(NH_4)_2SO_4$, urea, Cys, Lys,	MW	H_2O_2/HCO_2H	0.5 h	528
6	$(NH_4)_2SO_4$, amides, amino acids	UV	$K_2S_2O_8$	CFS	469
7	NH_4Cl, urea, EDTA, Ala, His, hydroxamic acids	UV	$K_2S_2O_8$	FIS	471
8	$(NH_4)_2SO_4$, urea, thiourea, amines, amides, amino acids	UV	$K_2S_2O_8$	FS, 8 min	484
9	Microbial C & N	-	$K_2Cr_2O_7$		516
10	Amino acids	MW	$K_2S_2O_8$	2 h	529

[a] Abbreviations: FS = Flow System; FIS = Flow Injection System; CFS = Continuous Flow System

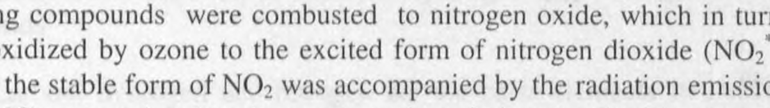
Table 6. Oxidative degradation of nitrogen-containing compounds by the „wet" procedures with subsequent reduction

No	Compound	Oxidative-reductive degradation				Literat.
		Oxidation	Conditions	Reduction	Conditions	
1	Hydrazines	$N \rightarrow NO_z$	H_2SO_4-H_2CrO_4 (200 °C)	$NO_z \rightarrow N_2$	Cu (500 °C)	381
2	Various nitrogen containing functional groups	$N \rightarrow NO_z$	H_2SO_4-H_2CrO_4; H_2SO_4-$KMnO_4$; H_2SO_4-KBr-$KBrO_3$ (20 – 200 °C)	$NO_z \rightarrow N_2$	Cu (500 °C)	421, 422

3	Oximes, semicarbazones, nitroani-lines, amino acids	N → NO_z	H_2SO_4 or H_2SO_4-H_2CrO_4 (20 – 200 °C)	$NO_z \rightarrow N_2$	Cu (500 °C)	443
4	Azoxy derivativ., triazenes, pentaza-1,4-dienes	N → NO_z	H_2SO_4 or H_2SO_4-H_2CrO_4 (20 – 200 °C)	$NO_z \rightarrow N_2$	Cu (500 °C)	444

2.2.3.1. Nitrogen Determination after Prior Oxidation to NO_2 and the Chemiluminescence Detection

In an alternative procedure of determination of nitrogen - the nitrogen-containing compounds were combusted to nitrogen oxide, which in turn was further oxidized by ozone to the excited form of nitrogen dioxide (NO_2^*). The return to the stable form of NO_2 was accompanied by the radiation emission (hν) (scheme 38), proportional to the concentration of nitrogen dioxide present in the gas combustion mixture.



$$S^* \longrightarrow \overset{CO_2 + H_2O}{\underset{NO}{+}} \xrightarrow{O_3} NO_2^* \longrightarrow NO_2 + h\nu$$

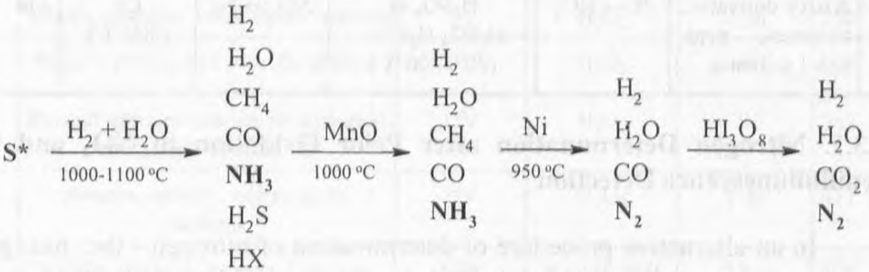
Scheme 38

The methods of nitrogen determination using the chemiluminiscence phenomenon presented the subject of a row of analytic reports [438,517,552,540]. The review on the methods of nitrogenous compounds determination occurring in air, using the effect of chemiluminiscence was written recently by Navas [502].

2.2.4. Nitrogen Determination by Hydrogenation Methods

The method of hydrogenization of samples containing nitrogen, belong to considerably less practical ones [80,120]. Its interesting modification, worked out by Ubik [347], depends on the pyrolysis of analyzed substance in a stream of hydrogen at temperature 1000-1100 °C. The pyrolytic products were passed through a layer of MnO, in which hydrogen sulfide and hydrogen halogenides were removed, and then over Ni at 950 °C, which caused the degradation of methane as well as ammonia to hydrogen and nitrogen.

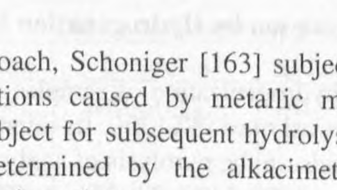
Carbon monoxide, present in the combustion products, becomes oxidized to dioxide (CO → CO_2) by means of HI_3O_8. The formed gas mixture was passed through suitable absorbers; by filling with anhydrone (removal of water) then with ascarite (removal of CO_2 as well as traces of hydrogen halogenides), and the remaining gas was introduced into a TCD detector (scheme 39).



Scheme 39

The method can be applied for nitrogen compounds, containing: C, H, N, O, S, Se, F, Cl and I, as well as Hg atoms.

In the alternative procedure (scheme 40) Stolyarow [491] subjected the analyzed samples to the exhausting hydrogenolysis (H_2—H_2O—Ni / 370 °C) converting the organic nitrogen to ammonia, subsequently determined potentiometrically with the use of iono-selective electrodes (NH_3 / NH_4^+).



Scheme 40

In a different approach, Schoniger [163] subjected nitrogen-containing compounds to decompositions caused by metallic magnesium. The formed magnesium nitride, was subject for subsequent hydrolysis (scheme 41), and the released ammonia was determined by the alkacimetric titration after prior distillation off from the reaction mixture.

$$S \xrightarrow{Mg} Mg_3N_2 \xrightarrow{H_2O} 2\,NH_3$$

Scheme 41

In the modified procedure of Lassaigne, Demirata [575] subjected the nitrogen-containing compounds to the reaction with metallic sodium (scheme 42).

$$S^* \xrightarrow[\text{Temp.}]{\text{Na}} \text{NaCN} \xrightarrow{(NH_4)_2S_n/H_2O} \text{NaSCN}$$

Scheme 42

The formed sodium cyanide was converted sequentially into thiocyanate, determined successively by complexometric titrations with Fe(III) ions.

3. Automatic Determination of Carbon, Hydrogen and Nitrogen in Organic Compounds

Carbon, hydrogen and nitrogen are the basic elements of structure of organic compounds and the most often determined in elementary analysis. Principle of their determination is based on destruction of organic substance on the way of oxidation to carbon dioxide and water, and their subsequent analysis. The first micro-method of determination of carbon and hydrogen, worked out by Pregl in 1912, was widely applied without larger modifications, by over three decades [25]. It was based on a slow combustion of analyzed sample in a stream of oxygen and involving the re-oxidation of the combustion products originally formed on the layer of lead chromate embedded on copper oxide. The formed ultimate gas products: carbon dioxide and water, were absorbed in the absorptive tubes, filled suitably with ascarite and magnesium perchlorate, and weighed before and after analysis [28].

The method of Pregl, and its modifications [28,254,272,370,391, were found to possess the essential limitations hampering the automation of the analytical process and making impossible its adaptation to the ultra-micro scale. For nitrogen-containing substance, the determinations results of carbon and hydrogen were not exact and the simultaneous determination of carbon, hydrogen and nitrogen, was not possible. A rapid development of organic chemistry implied the undertaking aimed at intensive investigations over automation of elementary analysis, shortening of the analysis time, lowering of the scale of determinability and also widening of the spectrum of determined elements [410].

A considerable shortening of the analysis time was achieved after the introduction to elementary analysis the method of instant combustion of sample. In this modification, the sample does not burn up successively by the use of movable furnace, but moves to the hot zone of combustion directly

[202,312,370,395], which permitted the partial automation of determination procedures.

The total automation of analytic methods became possible thanks to the development of gas chromatography [253,275,318,351,357] and its conjunction with the methods of elementary analysis [231,335,362,370]. It was effective when received with the replacement of the classical determinations in analysis of the combustion gas products (mass weighing, titration) - by the measurement of physical properties (proportional to the determined mass or concentrations), suitable to the automatic counting.

In measurements these physical magnitudes were used, which in studied area change to the determined chemical sizes directly, and in proportion to. In the automatic methods, the ultimate products of the combustion are most often analyzed by application of TCD detectors (Table 9).

3.1. Technical Foundations of Automatic CHN Elementary Analysis

3.1.1. Sample Combustion

Preparation of samples in the micro scale (to 1.5 mg), and particularly in the ultra-micro scale (< 1 mg), impersonates in elementary analysis important part. Homogeneous and dried to constant mass samples, are weighed out in metal containers (Al, Ag or Sn foil; 0.03 mm) of single use, and according the applied way of the combustion is mixed with oxidants, or without [385,394,395,410]. Volatile substances were introduced to the combustion tube, in sealed glass capillary tubes [325,385,394, 395,410].

In application of the micro-quantity scale to the combustion analysis, as well as the methods of high-sensitivity of measuring, the influence of sample conditioning in a carrier gas atmosphere before their introduction to analyzer, as well as maintenance of stable parameters of the apparatus regime, exert crucial role on the exactitude of results of analysis. The important stage presents also the way of introduction of samples to the analyzer. This is because it can cause a pressure fluctuation inside the apparatus, the same change of speed of gas carrier flow in the column, and in effect the disturbance of the work of TCD detectors. The automatic sample adapters with programmable time of individual operations assure to the apparatus assurance of the reproducible conditions of conditioning and insertion of the sample [410,414,417].

In automatic analyzers the combustion process should assure the total combustion of different types of organic compounds possibly quickly. The gas mixture comes into being as a result of sample combustion includes according from the sample composition the following gas components: CH_4, H_2, P_2O_5, SO_2, SO_3, H_2O, NH_3, NO_z. With the aim of their transformation into convenient for determination compounds (CO_2, N_2, H_2O), is necessary to conduct the additional oxidation ($CH_4 + CO \rightarrow CO_2$) and reduction ($NO_z \rightarrow N_2$) [317].

In the CHN determinations utilizing for the final measurements a TCD detection, in the apparatus occurs a dynamic conditions (combustion, carrier gas flow, automatic dosage of samples, etc.) and therefore the time of contact of initially gas formed products (products of pyrolysis and/or incomplete combustion) with oxidant layers is comparatively short (0.5 to 1 min). For this reason the combustion tubes are supplied with active oxidants, which convert quantitatively the gas products formed directly during combustion into convenient for chromatographic analysis the ultimate products (N_2, CO_2, and H_2O). In connection with this requirement wide spectrum of various oxidants were tested. Thus, since a long time a practical CuO [2,43,185] is also used in present analyzers [219,385,410]. The product of thermal degradation of silver permanganate, the so called catalyst of Koerbl, is very effective as the oxidant absorbing simultaneously sulfur and halogens. These properties are very convenient, however, constitutes the source of a quick deactivation of the oxidant [173,410]. Co_3O_4 oxidizes entirely and quickly hard burning organic substances in the temperature range 700-750 °C [96,185,236]. However, at temperatures over 800 °C underwent an irreversible transformation into less active CoO [247], presented no advantages in the comparison with CuO. Co_3O_4 is exceptionally resistant to the deactivation action exerted by phosphorus oxides nascent during the combustion of organophosphorus compounds [245].

Among other oxidative contacts deserve our attention MnO_2 [35,65,410], V_2O_5 410], $AgVO_3$ [410], WO_3 [206], $PbCrO_4$ [265], Cr_2O_3 [410] and CeO_2 [89,410], and also some composites [142,164,182,229,316], applied as the reactive fillings of the combustion tubes and/or applied as the oxidants added to the analyzed substance to capsule prior to the flush combustion. In the case of formation of compounds disturbing in the analysis (P_2O_5), it is necessary to absorb them initially on front layers of the reactive fillings [254,275,280].

An indispensable condition of obtaining a credible CHN results determination is the quantitative combustion of the analyzed sample [385].

There are methods of combustion in the static arrangement (the combustion runs in a closed space) [202,221,222], and the dynamic (combustion is carried out during constant movement of gases inside the apparatus) [74,75,82,210,326], in the atmosphere of oxygen [124,142,209,249,266,295, 345,352], or an indifferent gas with the addition of oxygen [210,410]. The injection of oxygen into the combustion space, with the gas continuous flow bearing [208,345], is also applied. It was used also the addition to combusted samples of some solid oxidants, releasing oxygen during their thermal decomposition [218,219,221,253, 281].

The most important methods of combustion applied for the analyzers conjuncted with gas chromatographs are presented in Table 7.

Table 7. Methods of combustion of organic samples applied in CHNSO analyzers conjuncted with gas chromatographic determinations

No	Methods of combustion	Determined elements	Sample mass [mg]	Combustion time [min]	Literature
1	Method of Dumas	C, H	2-8	20	186
2	Method of Pregl	C, H	2-6	20	265
		C, S	3-10	20-22	211
3	Combined methods of Pregl and Dumas	C, H, N	1	20	210
4	Method of Unterzaucher	O			205
5	Inductance furnace	C, H			196
		N	1-10	20	229
6	High-frequency inductance furnace	C, H, N	2-5		217
		C, H, N	0.3-1		274
		C, H	5-100 μl		272
		O, N			231
		N	1-10	20	229
7	Combustion bomb	C, H	8-11	17	202
8	Automatic combustion furnace of Sorgent	C, N, S	2 μl	3.5	271

The combustions carried out according to Dumas, Carius, Unterzaucher and Pregl, or by application of pyrolytic bombs (statical combustion) depends on a temporary stoppage of combustion gas products (cooled container), and subsequently their direct introduction into a gas chromatograph. A dynamic combustion according to Belcher [74,75], and/or Titov [82], later developed by Walisch [210] and Kozłowski [326], takes place in a continuous movement of the mixture of carrier gas and combustion products.

Both systems of combustion are applied in automatic analyzers, with adequate advantages and defects. The static arrangement applies a neutral gas (usually helium), in which atmosphere the sample is mixed with oxidant (e.g. CuO, Co_3O_4 or WO_3), creates the perfect conditions for instant combustion. During combustion of capsule foil delivers additionally the warmth, caused locally the substantial increase of the combustion temperature, favorable for the quantitative combustion of the analyzed samples.

The addition of oxidants to the analyzed sample, consists however, the source of bringing into the arrangement of gas components, identical with determined gas products derived from the sample combustion (CO_2, H_2O and N_2), and therefore the rise, not always constant blind test.

Apart from the combustion ways performed in the presence of oxidative contacts in form of metals oxides, acted as the oxygen donors, both in the atmosphere of oxygen and of the indifferent gas, the combustion in the atmosphere of oxygen with or without catalysts, were also applied [410].

The described above procedures of the sample combustions were found to possess a number of limitations. And so, a dosage of oxygen to the combustion zone of the tube is technically complicated [345], as well as requires the application of nitrogen-proof oxygen. The fulfillment of this condition requires additionally equipment of the applied gas chromatograph with a generator of oxygen [318,379].

The combustion of samples in the atmosphere of carrier gas, consisting mixture of helium-oxygen, permits a considerable simplification of the apparatus, and application for the analysis of TCD detection. The procedure requires, however, the application of preliminary removals of an oxygen excess from the combustion products, prior to the entry of analyzed gas to TCD.

The method employing the addition of oxidants to combusted sample, requires careful selection of suitable oxygen donors, and also stabilization of the combustion process as well as maintenance of a stiff regime of the apparatus work, regarding in calculation errors brought in by the applied oxidant. The method can not be applied for the combustion of hardly combustible substances due to their incomplete combustion [98].

The injection of oxygen to the combustion zone permits removal of these shortcomings and expands the list of compounds determined by this method [98,345]. For quantitative combustion of hardly combustible compounds the aluminothermy effect was alternatively applied [353,580]. For this purpose, the mixture of analyzed substance and oxidant was supplied with the components of aluminothermic mixture (the most often as the combination of Fe and Al_2O_3) prior to the combustion [429,580].

Presented in scheme 43 the course of strongly exothermic, the so called aluminothermic reaction [247], causes the local rise of the combustion temperature (metal container zone) about several hundreds degrees, and in effect, the intensification of the pyrolytic-oxidative processes, affording the quantitative total combustion.

$$Fe_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2\,Fe + 199\ \text{kcal}$$

Scheme 43

From analysis of the literature data results that, the addition of an oxidant to the analyzed samples presents the optimal solution. This procedure is useful in case of nitrogen determination as well as sufficient at determinations of C_xNH_y value, and was applied by Waśkowski in his dissertation work [614].

The problem of usefulness and utilization of different oxidants, reducers and catalysts in elementary analysis presents the subject of many investigations performed at present [213,343].

3.1.2. Physical Methods of Separation of Ultimate Gas Products of the Combustion

A principal condition of the elementary analysis influencing a choice of concrete road of the automation of analysis has to be fulfilled: the error of determination of every element can not exceeded 0.3 %, which puts on the requirement of exact stabilization of every parameters of the measuring arrangement.

The largest use in elementary analysis found the automatic methods originated from gas chromatography [248,261,368]. The use of a gas chromatograph for determination of such elements how the set CHNSO, influenced the simplification of many, formerly complicated analytical procedures [385]. The time of such analyses underwent substantial shortening with the maintenance of the standards of exactitude and repeatability in the comparison with the traditional analyses.

The gas chromatographs are equipped with columns for separation of the components of gas mixture, as well as recorders and integrators, servants to determination of individual components. These devices are without larger changes suitable for adaptation for needs of elementary analysis (in CH, CHN, CHNO as well as CHNOS combinations).

Kuck [186] was the first who turned attention to the possibility of usage of gas chromatography for elementary microanalysis. Duswalt and Brandt [265] elaborated out the method of chromatographic determination of carbon and hydrogen. This procedure applied the substance combustion in a stream of oxygen and was carried out in a tube containing layers of Ag and CuO. Water formed in the combustion, was subsequently converted into acetylene (reaction with calcium carbide), prior to the combustion products condensation in liquid nitrogen. The ultimate combustion products after the removal of oxygen were vaporized and subsequently analyzed chromatographically.

A different procedure of the CHN analysis was proposed by Sunberg and Maresh [201]. They burnt the samples in an anaerobic atmosphere, applying copper oxide as the oxidant and boundary strips of copper as the reducer. The absence of oxygen in the combustion products permitted on the additional determination of nitrogen, retention time of which on silica gel was identical with that exhibited by oxygen.

In other procedures for quantitative combustion of organic substances, Vogel and Quattrone [202] applied the addition of oxygen, when Reitsema and Allphin applied copper oxide [208].

Proposed methods of CHN determination with utilizations of gas chromatographs, required in every case substantial modifications or restructuring of the chromatograph outright [270].

The analytic conduct, though it shortened the time of individual determinations, was charged with a number of inconveniences. They were the requirements of frequent exchanges of calcium carbide which lengthened the total time of determination. Quantitative separation of the mixture of CO_2, H_2O and N_2, made the requirement of retention of CO_2 in liquid nitrogen, which complicated the automation of the analytic process. Additionally the combustion and also the chromatographic separation parameters were established by operator each time.

Despite the obvious limitations, the presented technical solutions made up the serious contribution into the investigation research over the adaptation of chromatographic techniques, for aims of elementary analysis. The review of representative works on this field is presented in Tables 9 and 10.

The reaction products formed during the degradation of organic substance can be separated in chromatographic columns by the method of out-washing (the predominant technique), displacing [410] or the method of frontal chromatographic analysis [360,381,421,443,444].

The out-washing method is the most practical method applied in elementary analysis, putting on columns the requirement of a quick and repeatable introduction of the combustion products. This condition is very hard to fulfill because introduced to the combustion tube substances have different chemical proprieties and can be supplied in different quantities also.

The dependence among height of the peaks of determined compounds and its concentration (function of concentration) is linear in a narrow range of the concentrations only, which results from linearity of the adsorption isotherm as well as the geometrical parameters of the column applied. The height of peak is dependent in relays of the temperature of the column, the speed of carrier gas bearing flow, how and a way of the introduction of a gas sample to the chromatographic system. Due to this, the contents of analyzed components are determined on the base of surface areas of corresponding peaks - measured by means of electronic integrators, working independently or in coupling with recorders.

The choice of suitable fulfillment of the chromatographic column for the effective chromatographic separation of gas combustion products, states the essential element of determinations in elementary analysis [385]. The suitable stationary phase of the chromatographic column is determined by the physico-chemical properties of the analyzed compounds, formed as a result of the processes of pyrolytical-oxidative degradation of samples combusted. The influence on the quality of chromatographic separation exerts a row of parameters such how the kind of used stationary phase, the composition and even the relative contents of separated components. And so, the partition chromatography is useful in an analysis of liquids and it does not find a larger use in the case of analysis of low-molecular gases. These are formed during the pyrolysis and subsequent combustion of the analyzed samples (CO_2, CO, CH_4, C_2H_2, H_2O, H_2, N_2), occurring during combustion analysis. This results from the fact, that the analyzed gases are faintly solvable in a majority of applied stationary phases, where are retained on the chromatographic column too briefly (low retention) to undergo the separation.

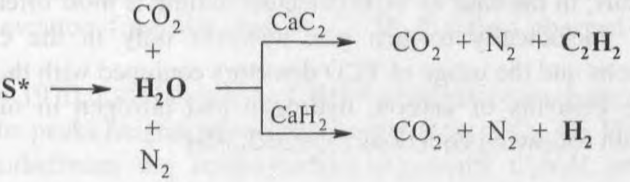
The representative chromatographic fulfillments applied for the analysis of combustion products and/or light hydrocarbons, used in the CHN elementary analyzers, are presented in Table 8.

Table 8. The representative chromatographic fulfillments applied in the CHN elemental analyzers

No	Fillings	Separated and determined components	Literature
1	Active carbon	CO	205
		CO_2, C_2H_2, N_2	274
2	Molecular sieve 5A	N_2	229,422
		CO, N_2	231
		CO_2, C_2H_2, N_2	217
3	Silica gel	CO_2, C_2H_2	201,265
4	Di-n-dodecyl phthalate on celite	CO_2, H_2	196
5	Di-n-dodecyl phthalate on infusorial earth	CO_2, H_2O	202
6	Poropak	CO_2, H_2O	455
		CO_2, H_2O, N_2	370,401,402,371
7	Poropak Q	CO_2, H_2, N_2	280,300
8	Poropak T	CO_2, H_2O, N_2, SO_2	411,447
9	Polypak	CO_2, H_2O, N_2	354,385
10	Polichrom A	CO_2, H_2O, N_2	403

The method of adsorptive gas chromatography, in which the process of separation is determined by the equillibria processes of sorptive gas - adsorbent interaction, presents the widest application method for analysis of low-molecular gases [286]. To the widest widespread chromatographic sorbents belong: carbon, molecular sieves, microporous silica and alumina oxide gels (Florosil, Porasil A and B), as well as microporous glass beds and polymeric compounds [334].

The execution of the elementary analysis determination moves to the quantitative combustion of the analyzed sample (CO_2, H_2O, N_2), the effective separation and subsequent quantitative determination of the separated combustion gas products by gas chromatography. The quality of separation of the analyzed components has direct influence on the exactitude of their determination. However, chromatographic separation of CO_2, H_2O and N_2, made up for a long time a serious problem to solution. Water - the strongly polar and highly boiling compound, differs in this respect from CO_2 and N_2, so that a quick, single-stage separation of CO_2, H_2O and N_2 mixtures, was practically impossible. Therefore water was tried to convert quantitatively into different compounds, in this into hydrogen (reaction with calcium hydride) or acetylene (reaction with calcium carbide) [scheme 44].



Scheme 44

Water was subject to the selective adsorption-desorption, or alternatively determined by use of two chromatographic column arrangements.

Really the use of new commercial polymeric fulfillments, obtained on the basis of copolymers of etylvinylbenzene and divinylbenzene, purchased under the brand name Poropak, afforded satisfied solution of the problem of chromatographic separation of mixtures of CO_2, H_2O and N_2. Another, commercially accessible polymeric fulfillment present: Polichrom A – a porous copolymer of styrene, more polar than Poropak how and Chromosorb 101 [375,401-403].

3.1.3. Determination of the Ultimate Products of the Combustion

For the analysis of ultimate products of substance combustion, namely the mixture of CO_2, H_2O and N_2, usually thermoconductive detection is complied (TCD). The principle of TCD working rely on a registration of thermal conductivity changes during the gases passage through measuring cells of the TCD detector, consequential with the thermal conductivity differences of the carrier gas applied and analyzed components. The highest thermal conductivity exhibit hydrogen and chemically passive helium, and these gases are usually used as carrier gas in gas chromatography.

Thermal conductivity detector (TCD) is sufficiently sensitive, reliable and comparatively inexpensive. TCD presents universal detector; detecting any presence of gas components (including CO_2, H_2O and N_2, also CH_4, CO, NO_z, H_2S, SO_2, etc.), with the sensitivity resulted from the thermal conductivity difference of analyzed component and the carrier gas applied. To make use of helium as carrier gas (the thermal conductivity higher 10 times than exhibited by CO_2), the TCD output signals keep in wide borders the linearity, the CO_2 content in a gas mixture, however, can not exceed 1 % [410].

The choice of bearing gas is closely connected with the type of applied detector. Thus, in the case of TCD detectors helium is most often applied, rarely argon, and episodically oxygen gas, however only in the case of the CH determinations and the usage of TCD detectors equipped with thermistors [410].

The contents of carbon, hydrogen and nitrogen in mass percentages accounts with following equations [350,363,398]:

$$\%\,C = I_C \times f_C / m, \quad \%\,H = I_{H}, \times f_H / m \ \text{ and } \ \%\,N = I_N \times f_N / m$$

where: I_C, I_H, I_N - the received number of impulses for CO_2, H_2 or N_2; the f_C, f_H and f_N - the empirical countable coefficients for carbon, nitrogen and hydrogen, determined during the combustion of standard substance with well-known content of these atoms, m - the mass of sample of burnt substance.

3.1.3.1. CHN Determination with Omission of Sample Weighing

At present, for the routine CHNSO determinations exclusively the commercial automatic analyzers are applied. The most numerous group of these examples consist apparatuses, in which the combustion products are determined using TCD detectors.

These analyzers require usually, ca. 1 mg range of sample quantities, which demand the application of an ultramicro-balance service [399]. According to Bobrański [385], service of this analyzers' type requires professional electronic subsidiaries, which is for many laboratories inconvenient. The list of representative, commercially accessible CHN elementary analyzers is presented in Table 9.

In the year 1961 Reitsema and Allphin [208], and later other explorers [301,304,341,383] published on the chromatographic method of determination of the *C* : *N* ratios, without of sample weighing. They introduced in a stream of helium the sample of substance, without weighing, to analyzer working in the system constructed in accordance with scheme 45.

Combustion tube → dryer → GC column (SiO_2) → TCD

Scheme 45

In measurements they obtained, the output TCD signals derived from CO_2 and/or N_2, and measured in the form of the corresponding surface areas were linear to the applied concentrations of analyzed components. The calculations after realization were received the coefficients, which did not directly reflect the real contents of % *C* and % *N* in the analyzed substance. Their values depended additionally on the working conditions of the whole apparatus, and therefore the method required calibration. Authors qualified the maximal deviation from the real % *C* / % *N* ratios; charged with errors of ± 0.25 %.

Rezl, in 1970, [304] using the CHN-1 elementary analyzer (CSSR), on the ground of the peaks heights of combustion products (CO_2, N_2, H_2O) assigned for analyzed substances the corresponding fragments $C_1N_xH_y$ and also the fragments H_1O_z. With obtained fragments, author enumerated the percentage contents of carbon, hydrogen, nitrogen and oxygen, and these data compared with theoretical. The determination error amounted 0.3 % for nitrogen and hydrogen and ± 0.3 % for hydrogen and carbon (at constant content of nitrogen). To marking the summarized formula of analyzed compounds it was necessary the acquaintance of molecular mass as well as percentage contents of the remaining elements.

Haeberli [341] repeated the experiment of Rezl, using the Carlo Erba CHN analyzer. Author presented the row of proportion coefficients, applied for calculation of the *C* : *N* : *H* ratios and for assignment of suitable indices of atoms comprised in the molecular formulas of analyzed compounds. Using the known *C* : *H* : *N* ratios, as well as the molecular mass and the percentage contents of remaining elements, he was able to assign the molecular formulas of analyzed substances.

The common feature of the methods elaborated by Rezl and Haeberli, was the elimination of weighing of analyzed samples. For determination of the

$C:H:N$ ratios, the Authors did not apply the rule of nitrogen [306], enabling in many cases delimitation from the $C:H:N$ relations of the real $C_xN_yH_z$ indices, exhibited in the molecular formula. The acquaintance of the remaining elements in the formula was not necessary in the analytical conduct.

In the work of Waśkowski [614] after delimitation of the $C:H:N$ ratios and application of the nitrogen rule, the real C_xNH_y fragment was enumerated without acquaintance of the full element composition of determined compounds. So far, to translate the *C, H* and *N* atoms ratio into the indices *x, y* and *z*, the Author [182,210] applied different proportion coefficients from which he enumerated the suitable indices. In the work of Waśkowski [614] it were proposed also three basic formulas, joining the number of atoms *C, N* and *H* in the molecular formula of determined compounds, with the values of electric output signals derived from TCD.

3.2. Principle of Working of Accessible Commercially CHN Analyzers

The introduction to trade automatic analyzers for elementary analysis stimulated strongly on development of elementary analysis. Meaningful illustration of this thesis presents literature searching of the past decades; for example in the base of Scientific Finder Scholar in period since 1961 to 2002 has stepped out near 600 works relating password *CHN analyzers*.

The profile of representative apparatuses for elementary analysis is presented in Table 9.

Table 9. Profile of representative elementary analyzers

No	Analyzer		Analysis[a]				Literature
	Producer	**Type**	**Atoms**	**Method**	**Sample [mg]**	**Time [min]**	
1	Kovo	CHN-1	C, H, N, S, (O)	C-GC (TCD)	0.5-3		393,455, 581
2	Carlo Erba	CHN–M 1104	C, H, N, S, (O)	C-GC (TCD)	0.1-3	7 (CHN); 5 (S); 6 (O)	349,442, 582
		CHN–M 1106	C, H, N, S, (O)	C-GC (TCD)	0.1-10[f]	7 (CHN); 5 (S); 6 (O)	
		NA 1500	C, N, S	C-GC (TCD)	0.5-100[f]	3 (N); 6 (NC); 10 (NCS)	

3	Thermo Finnigan[g]	Flash EA 3000 M 1112	C, H, N, S	C-GC (TCD)	0.01-1000[f]	5 (CHN) 15 (CHNS)	583
4	Perkin Elmer	PE 240	C, H, N	C-GC (TCD)	0.5-3		468,573
		PE 2400 Series II	C, H, N, S, (O)	C-GC (TCD)	0.1-500[f]	6 (CHN)	585
5	Leco Corp.	CHN-600	C, H, N	C-GC (TCD)	<200		596,598
		TruSpec CHN	C, H, N	C-A: DIR (CO_2); TCD (N_2)	<1000	4 (CHN)	597
6	Hewlett-Packard	F&M 185	C, H, N	C-GC (TCD)	0.5-0.8		590,591
7	Dani s.p.a.			C-GC (TCD)			458,599
8	Hereus	Heraus	C, H, N, S, (O)	C-GC (TCD)	2-4		385,586, 587
9	Technicon	Walisch-Technicon	C, H, N	C-GC (TCD)			263,280
		Technicon	C, H, N	C-GC (TCD)			373,592, 593
10	Euro Vector	Euro EA 3000	C, H, N, S, (O)	C-GC (TCD)	0.01-200[f]	3 (CHN) 10 (CHNS)	589
11	Exeter Analyt., Inc.	CE-440	C, H, N, S[b], (O)	C-GC (TCD)	1.0-500[f]	5 (CHN)	594
12	Elementar Analysensys-teme Gmbh	Vario EL III	C, H, N, S[c],(O)	C-GC (TCD)	1.0-800[f]	6-9 (CHN) 12 (CHNS)	588
13	Costeh Int. S.p.a.	ECS 4010	C, H, N, S[c],(O)				595

[a] Analysis applying chromatographic separation. [b] Analysis applying absorption. [c] Analysis applying absorption/desorption. [e] Oxygen analysis performed from separate sample. [f] Dosage from sample adapter. [g] Formerly Carlo Erba, now Thermo Electron Co.

The most representative concerned of Carlo Erba [349,377,442], Dani [458], CHN-1 (Kovo, CSSR) [393,408,412,422,443,444,455], CHN-2 [425], Technicon [263,280,311,373], Perkin Elmer [468], Leco [419,426,462,464, 470,480], Hewlett Packard [279,300,307,319,322,333,338,365,386,388,432, 461], or Yamagimoto [285] analyzers utilizations.

3.2.1. CHN Elemental Analyzer of Fisher

Ideological scheme of Fisher's Elemental Analyzer, constructed on the ground of Sundberg and Maresh investigations [201], is presented in Fig. 7.

The principle of working of an analyzer is following: an analyzed substance (1-5 mg), weighed out in the small boat, is mixed with Co_3O_4 and placed in the automatic sample feeder 1. The samples are introduced into a combustion zone of the combustion tube 2 successively, where in a helium atmosphere and temperature 900 °C undergo a pyrolysis-combustion processes. The combustion products are transferred in the stream of helium through a reactive filling of the tube 2, containing layers of metallic silver, copper oxide and metallic copper (Ag—CuO—Cu), respectively. During this passage, the processes of conversions of formed carbon monoxides into dioxide ($CO \rightarrow CO_2$) and derived from pyrolysis hydrogen into water ($H_2 \rightarrow H_2O$) on layers of CuO, as well as, the reduction of formed nitrogen oxides to nitrogen ($NO_z \rightarrow N_2$) on metallic copper (500 °C), occur simultaneously. At the same time, the other, potentially occurring products of the combustion, including halogens, hydrogen sulfide and phosphorus oxides, are chemically bounded on the layers of the reactive filling of the 2. Then, the gas mixture is passed through the water conversion column 5, where on a calcium carbide (CaC_2) layer, water vapor undergoes to acetylene conversion.

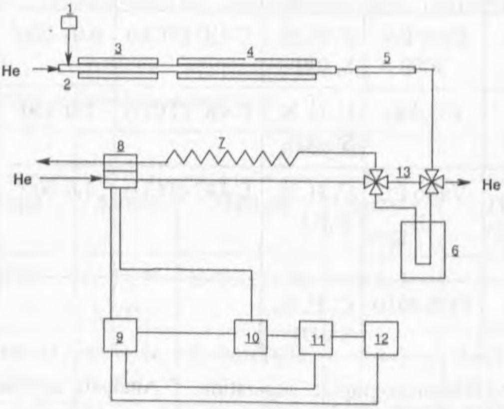


Fig. 7. Ideological scheme of CHN Elemental Analyzer of Fisher:
1 – sample adapter; 2 – combustion tube; 3 – movable furnace (900 °C); 4 – stationary furnace (500 °C); 5 – water conversion column (with CaC_2); 6 – dish with liquid nitrogen; 7 – chromatographic column; 8 – TCD; 9 – programming unit; 10 – counter; 11 – converter; 12 – printer; 13 – three-way bolts.

The transformed products of combustion (N_2, CO_2 and C_2H_2) are concentrated by a condensation-refrigeration in liquid nitrogen (6), prior to a separation on the chromatographic column 7. Signals from the thermal conductivity detector 8 (TCD), proportional to the concentration of detected components, are electronically processed, and then printed.

3.2.2. CHN Heraeus Elemental Analyzer

The Heraeus company [586,587] on the ground of Monar [250,331] and Merz [287] elaborations, designed the row of instrumental segments from which it was possible to assemble the CHNO analyzers working in various configurations (CH, CHN, N, CHNO). Ideological scheme of automatic CHN Heraus Elemental Analyzer is presented on Fig. 8.

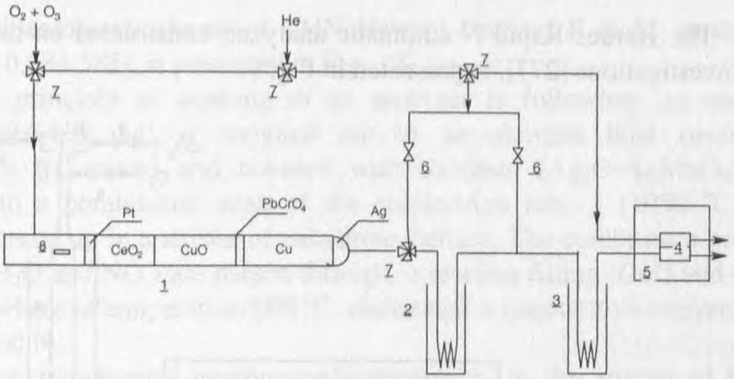


Fig. 8. Ideological scheme of automatic CHN analyzer of Heraus company [385,586,587]: 1 – combustion tube (650 °C); 2 – refrigeration/heating system (–70 °C to +300 °C); 3 – refrigeration/heating system (–60 °C to +51 °C); 4 – TCD; 5 – thermostat (60 °C); 6 and 7 – valve systems; 8 – boat.

The principle of working of an analyzer is following: an analyzed substance (2-4 mg) is weighed out in the platinum boat 8, placed into the combustion tube 1, and combusted in a stream of helium with an admixture of ozonized oxygen (ca. 50 ml). The combustion products (CO_2, N_2, H_2O, halogens, nitrogen oxides, sulfur and phosphorus oxides, as well as an excess of applied oxygen), are passed in the stream of carrier gas through a reactive filling of the combustion tube 1, over layers containing in turn, CeO_2—CuO—$PbCrO_4$—Cu—Ag. During this passage halogens, sulfur and phosphorus oxides are removed by chemical reactions with CeO_2 and $PbCrO_4$. On the copper layer an excess of oxygen is bounded ($Cu + O \rightarrow CuO$) and simultaneously nitrogen oxides undergo the reduction to nitrogen ($NO_z \rightarrow N_2$). The remaining products of combustion (N_2, CO_2, and H_2O) are passed in the stream of helium through the silver, cooled to temperature –70 °C ($CO_{2(s)}$

/iPrOH) coil tube 2 (water refri-geration), and next through the copper, filled with silica gel and cooled to temperature –60 °C coil tube 3 (absorption of CO_2 and partial absorption of N_2). After the sample complete combustion (5.5 min), the combustion segment 1 is disconnected from the measuring unit (2-5), and the subsequent desorption of absorbed in the coil tubes 2 and 3 compounds (H_2O, CO_2 and N_2) is successively carried out. Namely: nitrogen is quantitatively desorbed at +20 °C, carbon dioxide at +51°C, whereas water desorption requires +300 °C. The desorbed compounds are determined by the thermal conductivity detector 4 (TCD).

3.2.3. Heraus Rapid N Automatic Analyzer

The Heraus Rapid N automatic analyzer, constructed on the ground of Merz investigations [277], is presented in Fig. 9.

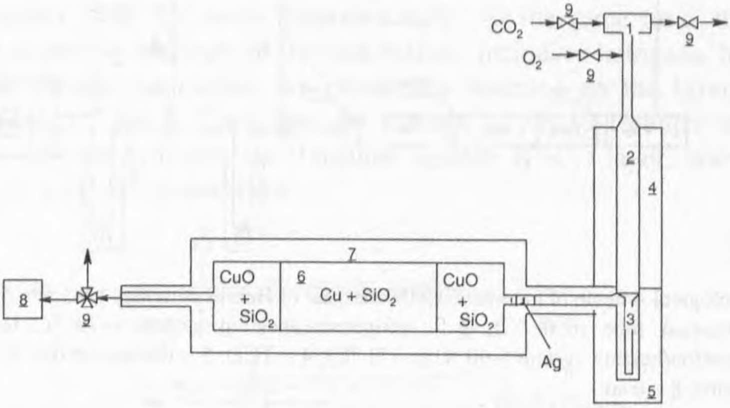


Fig. 9. Scheme of automatic nitrogen analyzer Heraus Rapid N:
1 – sampler; 2 – perpendicular combustion tube with a quartz insertion (1050 °C); 3 – perpendicular tube (950 °C); 4 and 5 – furnace of perpendicular tube with zone heating (1050 °C and 950 °C); 6 - horizontal tube; 7 – furnace of horizontal tube (500 °C) ; 8 – manostat; 9 – valves system.

The principle of working of an analyzer is following: an analyzed substance (20 mg) is weighed out in a metal container (Al or Sn foil), mixed and covered with a layer of the oxidant (CuO) and placed into a sampler 1. Air is evacuated from the sampler 1 by a flow of carbon dioxide, followed by an oxygen rinse of the combustion tube 2, for 1 min period. Hereinafter time, the sample is automatically transferred into the tube 2, where in temperature 1050 °C burns up instantly. After the combustion, a tributary oxygen flow is intermittently stopped and the installation is rinsed by a carbon dioxide stream.

The combustion products (CO, CO_2, H_2O and NO_z), are transferred in the stream of carrier gas through the tube 3 (filled with CuO–SiO_2 layer; 950 °C), then by the horizontal tube 6 [filled with Ag–(CuO + SiO_2)–(Cu + SiO_2)–(CuO + SiO_2) layers; 500 °C], where the quantitative oxidation of carbonaceous gases (CO → CO_2), the removal of an oxygen excess (Cu + O → CuO) and the reduction of nitrogen oxides to nitrogen by copper ($NO_z \rightarrow N_2$) take place. The carbon dioxide stream, containing molecular nitrogen, is steered to the azomat 8 (designed by Monar [237]), followed by an automatic gasometric measurement of a nitrogen volume.

3.2.4. CHN Elemental Analyzer of F & M Hewlett Packard, Model 185

An ideological scheme of CHN Hewlett Packard F & M, model 185 analyzer [410,584,585], is presented in Fig. 10.

The principle of working of an analyzer is following: an analyzed substance (0.6-0.8 mg) is weighed out in an alumina boat (using the microbalance 6), mixed and covered with oxidants (Ag_2O-$AgMnO_4$), and introduced to a combustion zone of the combustion tube 1 (1050 °C). The sample is burned up in a stream of anhydrous helium. The combustion products (CO, CO_2, H_2O and NO_z) are passed through a reactive filling (CuO and Cu) of the tube 1, where at temperature 500 °C, underwent a quantitative conversion to CO_2, H_2O and N_2.

These transformed combustion components, in the stream of helium carrier gas, are separated on the chromatographic column 4, and subsequently determined using the TCD (5).

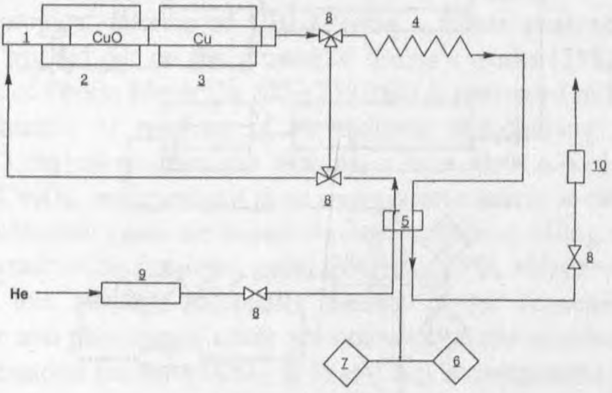


Fig. 10. Ideological scheme of CHN analyzer of Hewlett - Packard F & M model 185: 1 – combustion tube; 2 – electric oven (1050 °C); 3 – electric oven (500 °C); 4 – chromatographic column; 5 – TCD; 6 – recorder; 7 – microbalance of Cahn; 8 – cutting and/or three-way valves; 9 – absorber with anhydrous $CuSO_4$; 10 – rotameter.

3.2.5. CHN Elementary Analyzer of Technicon

Analyzer's function is based on the construction and procedure elaborated by Walisch [210,263,280]. The combustion process, as well as measurements (determination of CO_2, H_2O and N_2), are performed in a dynamic arrangement. Ideological scheme of CHN Elementary Analyzer of Technicon [385,410,592,593] is presented in Fig. 11.

The principle of working of an analyzer is following: an analyzed substance (0.3-0.4 mg) weighted out in a platinum boat is placed into a combustion zone of the combustion tube 1. Here, in a helium atmosphere enriched with 3 % of oxygen, the combustion is carried out. The combustion products (CO, CO_2, NO_z, N_2, H_2O, SO_z, X_2) are in the helium stream passed through a reactive filling (CuO—MgO—Ag) of the combustion tube 1, where in contact with CuO all carbonaceous components of the gas are converted into CO_2, and sulfur oxides and halogens are bounded by the silver-wool layer. The removal of an oxygen excess and the reduction of nitrogen oxides into molecular nitrogen are held in the reductive tube 3, over metallic, heated to temperature of 500 °C, copper. The stream of carrier gas after exit from the reductive tube 3, passes through the column 4, during which, water vapor becomes on a silica layer periodically absorbed. The formed by the water removal the gas mixture (CO_2 and N_2 in helium) is transferred to a chamber I of the TCD set 6, giving the total signal (CO_2 and N_2).

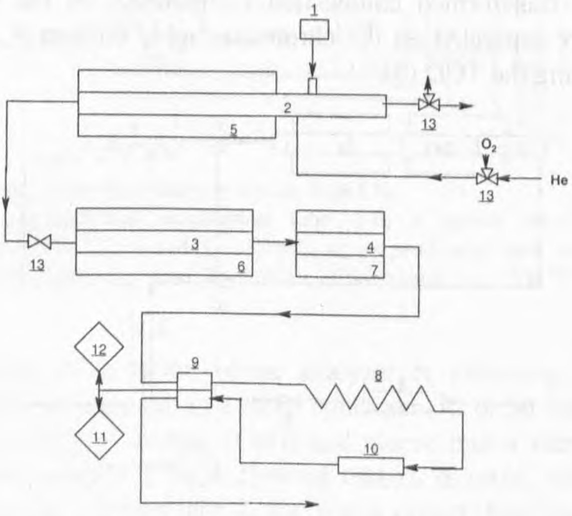
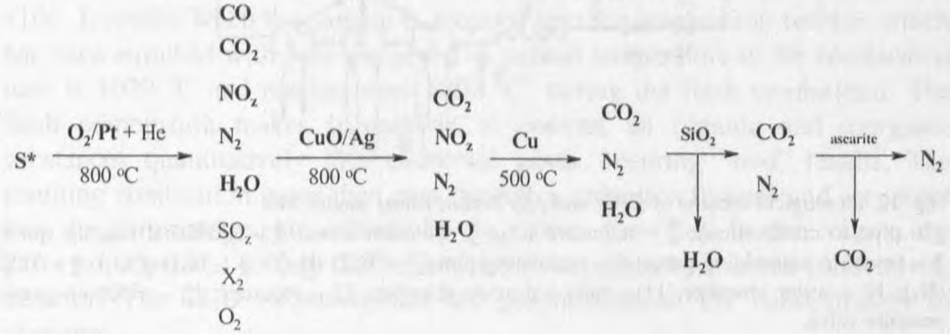


Fig. 11. Ideological scheme of CHN elementary analyzer of Technicon:
1 – sampler; 2 – combustion tube; 3 – reductive tube; 4 – drying column (SiO_2); 5 – electric furnace (800 °C); 6 – electric furnace (500 °C); 7 – electric furnace (up 300 °C); 8 – retardatory pipe; 9 – TCD; 10 – absorber for carbon dioxide; 11 – counter; 12 – integrator; 13 – valves.

This gas is passed then through the carbon dioxide absorber 7 (removal of CO_2 on a ascarite layer), next by the retardatory pipe 8, protractive the road of combustion gases. Here, thanks to the shift of forehead of strands of carbon dioxide and nitrogen (CO_2 and N_2) and carbon dioxide, water vapor and nitrogen (CO_2, H_2O and N_2), these do not overlap during the TCD chambers passage, and the analyzed products introducing the TCD chamber II give individual signal of nitrogen. After passage of nitrogen, the water absorber 4 is heated in aim of water desorption, followed by successive determination of water in the chamber I of the TCD. The chemical transformation occurring during analytical procedure, are presented in scheme 46.



Scheme 46

3.2.6. CHN Elemental Analyzer of Perkin Elmer, Model 240

An ideological scheme of CHN Perkin - Elmer analyzer model 240 [410,584,585], worked out on the ground of Simon's works [218,219,221,222] and the workers of Perkin Elmer Co. [253,259,281] is presented in Fig. 12.

The principle of working of an analyzer is following: an analyzed substance (0.5-3 mg) is weighed out in a silver boat, then mixed and covered with a layer of Co_3O_4, and burnt out in an oxygen atmosphere in the combustion tube 1. The combustion gases are passed through a reactive filling of the tube 1, including composed in the following order $CuO—Ag_2WO_4—MgO—Ag_2WO_4—Ag$ layers. During this passage potentially present in the combustion mixture halogens, sulfur and phosphorus oxide are bounded on the reactive filling. The mixture of combustion products (CO_2, H_2O and N_2) is transported in the stream of helium to the thermostated, previously evacuated to ca 1 mm Hg, vessel 5, where is homogenized and compressed to pressure 1500 mm Hg. The decompression is carried out through the copper coil pipe 6, acting as a sample valve. This volume is introduced to the previously evacuated measuring arrangement, consisting of three TCD sets (7, 8 and 9), in which in the gas circle between detector chambers, two absorbers were included. Namely, between the TCD 7 chambers - the absorber of water (10), and between the TCD 8 chambers – the absorber of carbon dioxide (11), respectively.

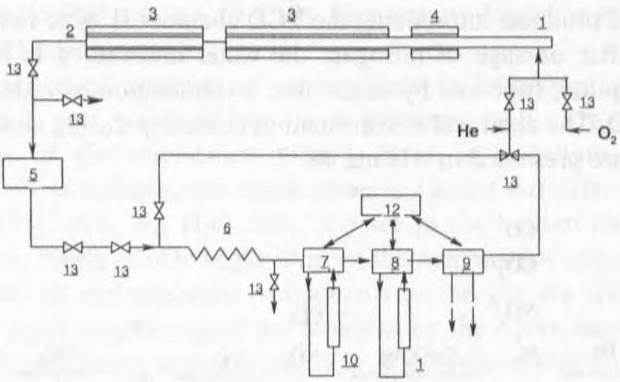


Fig. 12. Ideological scheme of CHN analyzer Perkin-Elmer model 240:
1 – pipe to combustions; 2 – reductive tube; 3 – electric oven; 4 – additional heating spiral; 5 – vessel to assembling gases; 6 – retardatory pipe; 7 – TCD (H_2O); 8 – TCD (CO_2); 9 – TCD (N_2); 10 – water absorber; 11 – carbon dioxide absorber; 12 – recorder; 13 – electromagnetic pressure valve.

Therefore the output signal coming from the TCD 7 corresponds to the water content; from the TCD 8 – corresponds to carbon dioxide content and from the TCD 9 – corresponds to the nitrogen content, respectively. The signals sent from TCD sets are recorded on graph in form of right lines, corresponding to H_2O, CO_2 and N_2, which amplitudes are proportional to these components concentrations in the carrier gas. After loading of samples adapter, the whole process runs automatically. The analyzer is equipped with an automatic balance of Cahn, as well as a computer for results calculation.

3.2.7. CHNS(O) Elemental Analyzers of Carlo Erba

The family of manufactured by Carlo Erba company Elemental Analyzers, consists of the series of outstanding quality instruments. This contains: the EA model 1100, introduced on the market in 1968 and being the first fully automated CHN-O Elemental Analyzer, the CHN-O EA model 1104 (1970) - equipped with autosampler and combustion tube furnace vertically oriented, the CHN-O EA model 1106 (1975) - adapted to wide range CHN-O determinations (from 100 ppm to 100 %), and, introduced on market in 1988, the EA model 1108 - adapted for simultaneous CHNS-O determinations. Flash

EA1112 - the newest product of the Company, present the compact, highly computerized instrument, with computer controlling of oxygen dosage.

Ideological scheme of CHNS Elementary Analyzer of Carlo Erba, model 1106 [402,582, 583], constructed on the ground of former investigation of Pella and Colombo [278,292,345], is presented in Fig. 13.

The operating principle

The elemental Analyzer model 1106 provides: instantaneous combustion due to the low mass of the system and exothermic oxidation of the tin sample container which falls directly into the hottest zone of the reactor. “Flash combustion” of the sample in the combustion reactor is a key feature of the EA 1106. It results when the sample is dropped into the combustion reactor, which has been enriched with pure oxygen. The normal temperature in the combustion tube is 1020 °C and reaches over 1800 °C during the flash combustion. The flash combustion makes it possible to convert all organic and inorganic substances quantitatively into elemental gases, ensuring “real” results. The resulting combustion gases then pass through a reduction furnace and are swept into the chromatographic column by the carrier gas (He). In the column the gases are separated so they can be detected in sequence by thermal conductivity detector. The TCD output signals are proportional to the concentration of elements.

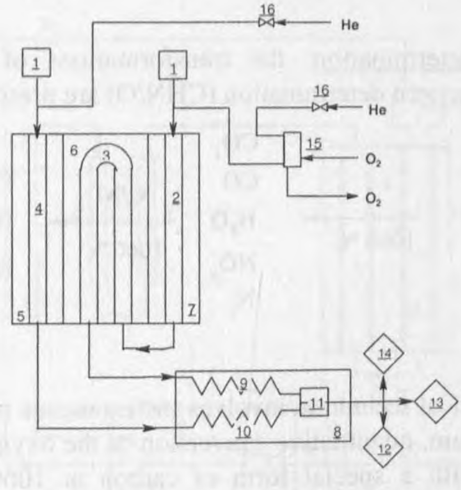
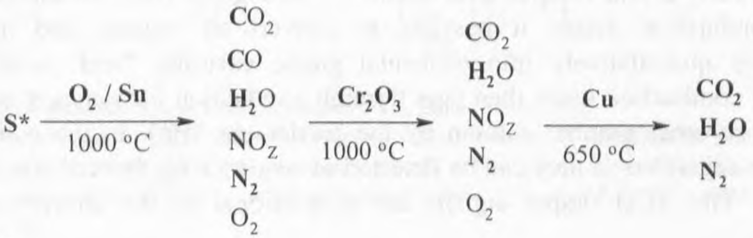


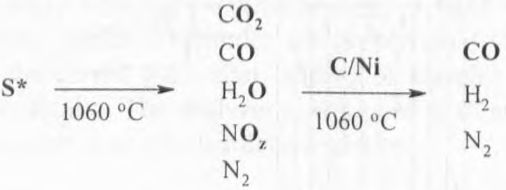
Fig. 13. Ideological scheme of elemental analyzer (CHNOS) of Carlo Erba M 1106: 1 – samplers; 2 – combustion reactor (CHN); 3 – reduction reactor (CHN); 4 – pyrolysis/combustion reactor (O/S); 5 – pyrolysis/combustion furnace; 6 – reduction furnace (CHN); 7 – combustion furnace (CHN); 8 – thermostatic oven; 9 – chromatographic column (CHN); 10 – chromatographic column (O/S); 11 – TCD; 12 – recorder; 13 – integrator; 14 – computer; 15 – oxygen injection multi-way valve; 16 – cutting off bolts.

CHN determination: the organic samples are weighed into tin containers and dropped at preset times into the vertical quartz tube 2, heated at 1010 °C, through which a constant flow of helium is maintained. When a sample is introduced, the helium is temporarily enriched with pure oxygen. Flash combustion takes place, primed by oxidation of the container. Quantitative combustion is then achieved by passing these gases over Cr_2O_3. The mixture of combustion gases is passed through the reduction reactor 3 filled with copper at 650 °C to remove the excess of oxygen as well as reduce of nitrogen oxides to nitrogen. Then formed gas mixture is introduced to the Poropak QS chromatographic column 9 heated at about 100 °C. The individual components are then separated, eluted in the order $N_2 > CO_2 > H_2O$, determined by TCD and recorded. The transformations of analyzed substances occurring during CHN analysis are presented in scheme 47.



Scheme 47

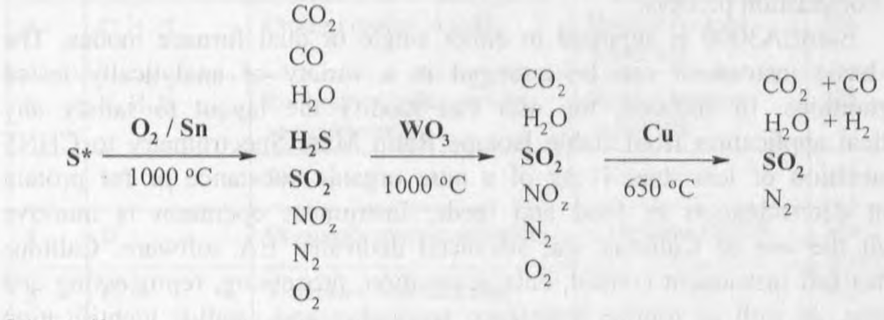
Oxygen determination: the transformations of analyzed substances occurring during oxygen determination (CHN/O) are presented in scheme 48.



Scheme 48

The analytical technique involves instantaneous pyrolysis of the sample in a stream of helium, quantitative conversion of the oxygen-containing gases to CO on contact with a special form of carbon at 1060 °C and quantitative separation of the CO formed, from the mixture by gas chromatography.

Sulfur determination: the samples, weighed into tin containers, are introduced at preset time into the quartz reactor 4 heated at 1000 °C, through which a constant stream of helium is maintained. When the samples fall the helium stream is temporarily enriched with pure oxygen. Qualitative conversion to SO_2 is then achieved by passing the gases over copper, the mixture is introduced into the chromatographic column 10 heated at 100 °C, where SO_2 is separated from other combustion gases. The transformations of analyzed substances occurring during sulfur determination (CHN/S) are presented in scheme 49.



Scheme 49

3.2.8. CHNS(O) Elemental Analyzer EURO EA 3000

Ideological scheme of analyzer of EuroEA3000 manufactured by Eurovector [589] is presented in Fig. 14.

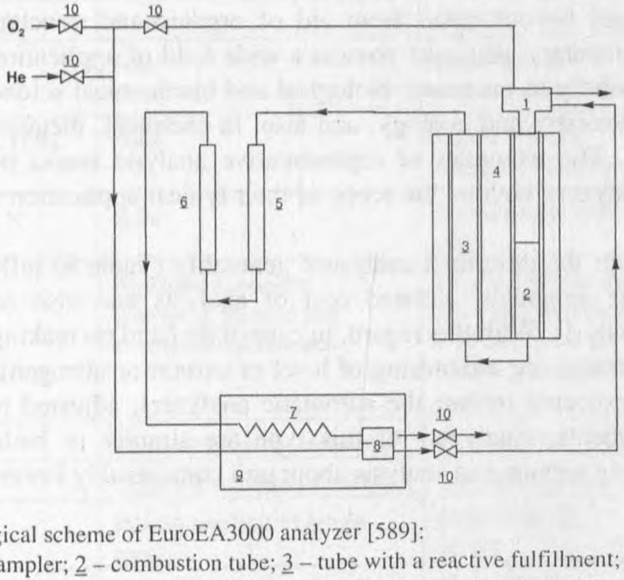


Fig. 14. Ideological scheme of EuroEA3000 analyzer [589]:
1 – automatic sampler; 2 – combustion tube; 3 – tube with a reactive fulfillment; 4 – oven; 5 – tube with a reactive fulfillment; 6 – tube with a reactive fulfillment; 7 – chromatographic column; 8 – TCD; 9 – thermostat; 10 – valve.

A compact, fully automatic elemental analyzer for determinations of CHNS-O, represents a quantum leap in oxygen pyrolysis and state of art of CHNS dynamic flash combustion. It is based on an innovative operating principle which allows for sample specific oxygen dose volume, and also offers independently programmed dosing rate, providing for full flexibility and control of the combustion process.

EuroEA3000 is supplied in either single or dual furnace modes. The same basic instrument can be arranged in a variety of analytically tested configurations. In addition, the user can modify the layout to satisfy any analytical application from stable Isotope Ratio Mass Spectrometry to CHNS determination of less than 1 mg of a pure organic substance or for protein content determination in food and feeds. Instrument operation is intuitive through the use of Callidus, the advanced dedicated EA software. Callidus provides full instrument control, data acquisition, processing, reprocessing and reporting, as well as routine maintance prompting and catalyst identification with configuration-specific part number codes shown on-screen.

3.3. Application of Elementary Analyzers in Environmental Analysis

Generality of modern elementary analyzers (the possibility of simultaneous multielemental determination, in these of carbon, hydrogen, nitrogen, sulfur, oxygen and halogens) causes, that field of application of these instruments goes beyond apart from aid of organic and structural chemistry scope. The elementary analyzers possess a wide field of application in analysis, directed particularly to medicine, biological and biochemical sciences, food and agricultural chemistry and ecology, and also, in chemical, metallurgical and/or mine industry. The examples of representative analytic works on the use of elementary analyzers' beyond the scope of their typical application are presented in Table 10.

However the described analyzers' generality (Table 8) influences at the expense of the apparatus, isolated cost of analysis and also on speed and precision of analysis. With this regard, in case of demand on making analyses' of one type of element (eg monitoring of level of carbon or nitrogen), analyses' of this type are executed by use the automatic analyzers, adjusted to analysis of individual elements. Analyzers of this type are simpler in building, and so cheaper, offering service and analysis about unit considerably lower costs.

Table 10. Application of elementary analyzers for environmental and industrial analysis

No	Determined element	Origin of analyzed sample	Analyzer	Literature
1	C	Particulate organic carbon	Hewlett Packard model 185	283
2	C, H, N	Crushed rocks and solids	Hewlett Packard model 185	328
3	C, H, N	Refractory nitrides, carbides and carbonitrides	Hewlett Packard model 185	338
4	N	Soil	Technicon	373
5	O	Organophosphorus pesticides	Carlo Erba CHNO	409
6	C, N	Sediments, sediment trap materials, plankton		413
7	C N	VC, NbC, TaC Soil	CHN-3	424
8	N	Fertilizers	CHN-1	422
9	C, N	Soils	Leco CHN-600	426
10	C	Analysis of geological materials	Yanaco-CHN corder	
11	C, H, S	Soils	CHN-60	461
12	C, N C, H, N	Soils	Leco-CHN-600 elementary analyzer	463
13	TOC, TON,	Soils	Leco-CHN-600 elementary analyzer	471
14	C, H, N	Soils	Perkin Elmer 2400 CHN	469
15	^{15}N	Agriculture research, biological, medical and environmental research	FP 228, CHN 89.00, NA 1500, Roboprep – all coupled with NOI-6 15 analyzer system	465
16	C, N	Carbonate-bearing sediments	Yanaco MT-5	483
17	N	Crude oil and heavy distillate	CHN-O-Rapid	534
18	C, H S	Routine analysis of brown coal	CHN-1000 EA SC-32	460
19	N, C	Trace analysis of coal and nitrogen in plants and soils	CHN EA	454

20	C, H, N	Particulate carbon in water	CHN-EA	355
21	C, H, N, O, S	Elemental analysis of solid and liquid fuels for determination of their caloric value	CHN-EA	427
22	C	OC In marine sediments	CHN-EA	430
23	C, N	Determination of relationships between biomass and biovolume of naturally derived bacterio-plankton	CHN-EA	432

The several automatic analyzers for such determinations, in these carbon analyzers (TOC, OC, TIC), nitrogen analyzers (TN, TON), sulfur analyzers (TOS, TS) and analyzers for determination of halogens (TOX, TX) are described in review work of Namieśnik [440].

4. Methods of Determination of Carbon and Nitrogen in Environmental Samples

4.1. Methods of Environmental Carbon Determination

The determination of carbon, apart from the CH analyses performed in elemental analysis of organic compounds [**& 2.1**, **& 3.**] belongs also to the subjects of interest in environmental [440,479, 484,570], industrial [536,545], and biological and related [407,468,516,535,552] fields.

Thus, the carbon content in soils is the one of major factors determining soil fertility. In result, many papers have been published on its determination in soil [426,457,462,468,470, 500,519,525,527,543,544,554,559,565,572], as well in marine sediments [515,524,531] recently. Several papers were on the various carbon determinations in environmental samples published, including atmosphere [361,387,390,394,418], aqueous media [320,336,348,357,358,376, 377,384,440,453,484,485,488,490,506,512,542,548,549,569,570], rocks [294, 505] and environmental sediments and suspensions [359,377,378,431,524, 535,550].

The determination of carbon in environmental samples can concern of the total carbon (TC), the total organic or inorganic carbon (TOC or TIC), the dissolved carbon (DC) and the purgeable or non-purgeable organic carbon (POC or NPOC), respectively. The review on the total parameters describing environmental pollution was recently by Namiesnik written [437].

The determination of carbon in environmental samples, is usually performed using one of the following methods:

- by infra-red reflectance spectroscopy [547,554,567] or non-dispersing IR [337];
- by inductively-coupled plasma emission spectrometry [544,556];
- by microwave-induced-plasma atomic emission spectrometry [534];
- by particle-hollow cathode atomic-emission spectroscopy [510];
- by wavelength-dispersive X-ray analysis [486,545];
- by radiochemical methods [374,475,503,505,546,567];
- by Mass Spectrometry [407,492,522];
- by thermal-optical methods [496].

The determination of TOC usually relay on the oxidation of carbon-containing samples (directly or after preliminary concentration [440]) to CO_2 and its subsequent determination, or on the basis its prior conversion into methane, subsequently determined. The possibly determination of CO_2 can be utilizing one from the following methods conducted:

a. determination of CO_2 by means of IRD [358,459] or utilization flame IR emission (FIRE) [445];
b. by prior reduction of CO_2 into methane with sequent determination of methane using FID [320,336,389];
c. gravimetrically [309] or turbidometrically [564];
d. by spectrophotometrical methods [434,450];
e. by electrochemical road, in this by potentiometric [435,492] or conductometric [433, 451,452,490] titration;
f. by inductively coupled plasma - atomic emission spectrometry (ICP - AES) [420].

The comprehensive review on the methods of carbon dioxide determination, was recently by Robards published [474].

The precursor of UV usage in the mineralization of organic compounds is Armstrong [252, 440]. This technique was the subject of further, more detailed investigations on the quantitative conversion of organic carbon to CO_2, including the influence of such factors as UV lamp power, pH, kind and quantity of the oxidant added, temperature and time of radiation [394,395,404,484].

The modification of the UV-degradation method, by application of a UV-degradation in flow, introduced by Goulden and Brooksbank [358], found the wide use in trade TOC analyzers [450,452,459]. The method of UV-promoted degradation of carbon-containing samples into CO_2 was the subject of review works of Namieśnik [440], Robards [474] and Golimowski [484].

The first instrumental method of the total carbon determination (TOC) was described in 1963 by Van Hall [224], and applied the high-temperature-combustion (HTC: O_2, catalyst, 900 °C) of organic substances occurring in water samples to CO_2, subsequently determined by means of IRD.

Table 11. Determination of carbon in biological and environmental samples using high temperature combustion methods

No	Determination of carbon in environ-mental samples	Conditions for HTC of carbon in environmental and biological samples	Carbon determination (apparatus)	Litera-ture
1	TOC (in soil)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2/cat; 680 °C)	IRD	513
2	TOC, TON (in surface water)	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{NO_z} + H_2O$ (O_2/cat; 680 °C)	IRD CHLD^b (NO_z	540
3	OC (in soil)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2/cat; 840 °C)	(LECO CR-12)	525
4	DOC	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (Pt/Al_2O_3; 800 °C)	IRD (CO_2)	508
5	TOC (in solid matters)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2; T > 1300 °C)	ND-IR	558
6	TC, TOC, TON (in solids)	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{NO_z} + H_2O$	(EA 3000)	541
7	TOC, TON (on filters)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (Co_3O_4)	Elemental and isotopic analysis	520
8	TOC, TNB (in water)	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{NO_z} + H_2O$ ($O_2/Mo/SiO_2$; 690 °C)	IRD (CO_2) CHLD^b (NO_z)	540
9	TC, TIC, TOC (in water)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2/Pt; 800 °C)	(Analytic Jena)	549
10	Marine DOC	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ [O_2 (580 °C); CuO-MnO_2 (450 °C)]	IRMS	485
11	Standardization of old whiskey	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$	GC-IRMS	522
12	Radiocarbon dating	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2/Pt; 800 °C)	Radioactivity measurement	492
13	TOC (in water)	$S^* + O_2 \rightarrow \mathbf{CO_2} + H_2O$ (O_2/Pt; 900 °C)	IRD	224
14	OC, TC, TN (in soil)	$S^* + O_2 \rightarrow \mathbf{CO_2} + \mathbf{NO_z} + H_2O$ (1040 °C [OC] or 1300 °C [TC,TN])	IRD (CO_2) TCD (N_2)	559, 570

15	TOC (in soil)	$S^* + O_2 \rightarrow CO_2 + H_2O$ (O_2/Pt; 690 °C)	IRD	540
16	TOC (in water)	$S^* \rightarrow CO_2 \rightarrow CH_4$ (A: O_2/Pt; 900 °C; B: H_2/Ni; 400 °C)	FID	320
17	TOC (in water)	$S^* \rightarrow CO_n \rightarrow CH_4$ (A: 850 °C; B: H_2/Ni; 350 °C)	FID	336

[a] Abbreviations: S* = sample; IRMS = Isotope Ratio Mass Spectrometry; IRD = Infra Red Detector; FID = Flame Ionization Detector; CHLD = Chemiluminiscence Detector. [b] CHLD: $NO + O_3 \rightarrow NO_2^* \rightarrow NO_2 + h\eta$.

In the later period, the low-temperature combustion methods (LTC, wet combustion), were applied with the use for oxidation of the peroxydisulfate reagent and UV radiation, alone or in conjunction. The examples of carbon determinations in different environmental samples, using the various HTC and LTC procedures, are in Table 11 and 12 respectively presented.

In connection with the dissemination of drinking water by chlorination, necessary at present are the methods enabling on the sensitive determination of volatile trihalometanes (POC) in presence of other not volatile carbon compounds (NPOC). The representative solution of this problem was in the analyzer of Envirotech–Dohrmann applied. This analyzer, is schematically presented in Fig. 15.

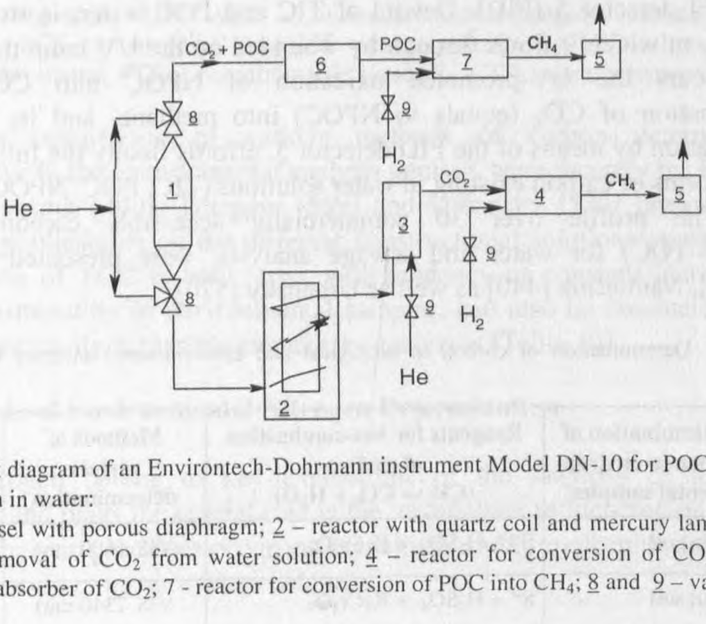
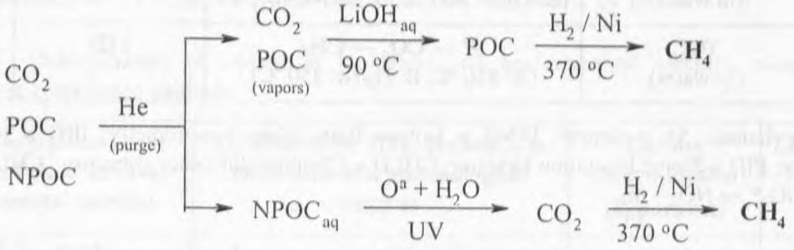


Fig 15. Block diagram of an Environtech-Dohrmann instrument Model DN-10 for POC and NPOC determination in water:
1 – glass vessel with porous diaphragm; 2 – reactor with quartz coil and mercury lamp; 3 –glass vessel for removal of CO_2 from water solution; 4 – reactor for conversion of CO_2 into CH_4; 5 – FID; 6 – absorber of CO_2; 7 - reactor for conversion of POC into CH_4; 8 and 9 – valves.

The chemical transformations, being the basis of the determination described, are presented in scheme 50.



[a]Oxygen introduced in the form of aqueous solution of peroxydisulfate

Scheme 50

The principle of working of an analyzer is following: a sample of analyzed water (10 ml) is mixed, in the glass reactor 1 stocked with a porous diaphragm, with an acidified solution of the peroxydisulphate reagent. A helium stream, passing through the porous diaphragm of the reactor 1, washes CO_2 (TIC) and volatile carbon compounds (POC) into the carbon dioxide absorber 6 (LiOH, 90 °C), and then to the reductive reactor 7 (H_2 /Ni; 400 °C). The conversion of POC to methane occurs here, which is successively determined in the cell of detector 5 (FID). Devoid of TIC and POC water, is steered to the reactor 2, in which it flows through by wounded on the UV lamp the pipe coil. Here occurs the UV-promoted oxidation of NPOC into CO_2. Further transformation of CO_2 (equals to NPOC) into methane, and its subsequent determination by means of the FID detector 5, affords finally the full analysis of various forms of carbon existing in water solutions (TIC, POC, NPOC).

The profile over 30 commercially accessible carbon analyzers (TC–TIC–TOC) for water and sewage analysis, were presented by Becker [376,383], Namieśnik [440] as well as Urbansky [570].

Table 12. Determination of carbon in biological and environmental samples by prior wet-oxidation

No	Determination of carbon in environmental samples	Reagents for wet-combustion of carbon ($CH \rightarrow CO_2 + H_2O$)	Methods of carbon determination	Literature
1	OC in soil	$S^* + H_2SO_4 + K_2Cr_2O_7$	VIS (600 nm)	536
2	OC in soil	$S^* + H_2SO_4 + K_2Cr_2O_7$	VIS (340 nm)	527

3	TOC in soil	$S^* + H_2SO_4 + K_2Cr_2O_7 + Ag_2SO_4$; MWD	Titration of Cr^{+6} with Fe^{+2}	524
4	Microbial carbon and nitrogen	$S^* + H_2SO_4 + K_2Cr_2O_7$; 144 °C, 3 h	VIS	516
5	Marine DOC	$S^* + H_2SO_4 + H_2O + CuCl_2$; SCS (650 °C, 350 barr)	MS	515
6	TOC in water	$S^* + H_2SO_4 + K_2S_2O_8 + AgNO_3 + H_2O$; UV, 80 °C, 20 min	PTR, CTR	490
7	RCC in biological and environ. samples	$S^* + HNO_3$	MIP-AES	537,560
		$S^* + HNO_3 + H_2O_2$; HPMWD		
		$S^* + HNO_3 + O_3$; HPMWD		
		$S^* + HNO_3 + HClO_3 + HClO_4$; HPMWD		
		$S^* + HNO_3 + HF$; HPMWD		
8	TOC	Electrochemical oxidation ($C + 2 H_2O \rightarrow CO_2 + 4 H^+ + 4 e$)	ED	504
9	TOC	$S^* + O_2 \rightarrow CO_2$ Closed Loop Technology		553

Abbreviations: S^* - sample; MWD – microwave digestion; HPMWD – high pressure micro-wave digestion; MIP AES – microwave-induced-plasma atomic emission spectrometry; SCS – supercritical state; MS – mass spectrometry; UV – ultraviolet; VIS – visual spectrometry; PTR – potentiometric titration; CTR - conductometric titration, respectively.

The comparison of various methods of carbon determinations, representative in the environmental analysis applied, were recently by Takahashi [336], Namieśnik [440], Traegger [569] and Urbansky [570] presented. The number of publications on the different constructional solutions applied in the determination of TOC is very large, with tendency of constant increase. The carbon determination in environmental samples, can also be conducted by the use of commercially accessible elementary analyzers [Table 10].

4.2. Methods of Environmental Nitrogen Determination

Nitrogen belong to key-heteroatoms of the majority of bioorganic compounds and plays the crucial role in the metabolism influencing on intensity of the metabolytic processes occurring on cellular and/or molecular level [537], and therefore affecting ecosystem balances.

Therefore, the determination of nitrogen content in various environmental samples considered as a major parameter of their utility, purity or fertility, presents the problem of importance of modern ecology. An isotopic ratio of nitrogen can be useful as the tool for transformation of soil nitrogen studies [518]. Thus, the content of nitrogen in soil [373,426,437,439,457,462, 468,470,491,500,559,561,572] and fertilizers [370,374,422,436] consists the measure of their fertilization, in plants [345,400,403,427,438,448] and agricultural and food products [371,436,446,495,507,511,514,522,526,532,551, 552,566,575,577,580] - as the measure of protein content and nutrition value, in biological samples - as the important factor influencing on health of investigated tissues or organisms [431,444,459,476,516,530,535,561]. In addition, the analysis of nitrogen content in environmental samples, especially in aqueous media [382,438,478,484,491,501,512,529,540,555,563], rocks [505], petroleum [143,533], various suspensions [550] and coal ashes [434] supplies in the important from ecological view factors.

In the case of determination of the pollution degree of environment, the determination of total nitrogen content (TN) in air, water and savages, and soil can provide a number of valuable data for agrochemical science, especially, in the range of utilization of nitrogen by plants in the considered eco-system. The majority of popular trade nitrogen analyzers [521,562,579] work on the base of the prior quantitative degradation (HTC or LTC) of nitrogen-containing organic compounds [579] into nitrogen oxides (or nitrogen) or ammonia, and subsequent automatic determination of the formed compounds.

In dependence on the applied detection method, the determination of nitrogen in environmental samples is performed usually by means of:

1. Analyzers equipped with chemiluminescence's detector (Antek Instruments Inc. [600-603]; Digital Nitrogen Analyzer Models: 703 B, 703 C and 720; Envirotech-Dohrmann [608-610]; Total Nitrogen Analyzer Models: DN-10 and DN-100; Mitsubishi Chemical Industries Ltd. [611-613]: Total Nitrogen Analyzer Model TN-05).
2. Analyzers equipped with coulmetric detectors (Envirotech-Dohrmann: Microcoulometric Titration System Model MCTS-10 [608-610].
3. Analyzers equipped with TCD [572,596-598,604-607] and/or IRD detectors [563].

4.2.1. Total Nitrogen Analyzer of Envirotech-Dohrmann, Model DN-10

The representative analyzer for the TN determination in environmental samples, is schematically presented in Fig. 16.

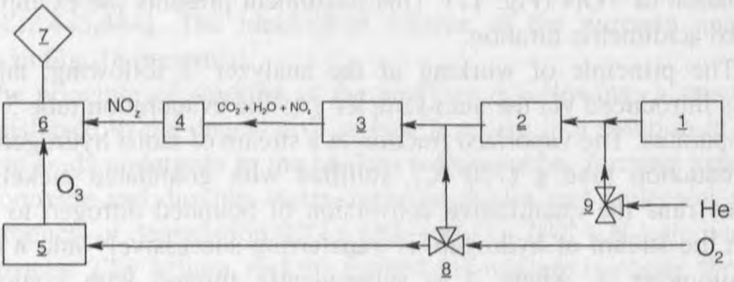
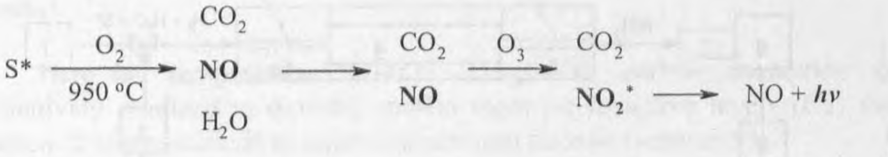


Fig. 16. Schematic diagram of a design of a DN-10 Total Nitrogen Analyzer product by Envirotech-Dohrmann for analysis of solid and liquid substances and/or their solutions [559]: 1 – microsyringe for gas/liquid sample or a boat system for solids; 2 – vaporization tube (700 °C for liquids or 900 °C for solids); 3 – oxidation tube (900 °C); 4 – water and CO_2 absorber; 5 – ozone generator; 6 – chemiluminescence's detector; 7 – integrator; 8 and 9 – valve systems.

The principle of working of an analyzer is following: a sample is introduced into the vaporization tube 2 (700 – 900 °C) of the analyzer, where undergoes the pyrolytic degradation into volatile gaseous products, which are directed into the combustion tube 3, where in an oxygen atmosphere at temperature 950 °C are combusted into CO_2, H_2O and NO_z.



$$S^* \xrightarrow[950\,^{o}C]{O_2} \begin{matrix} CO_2 \\ NO \\ H_2O \end{matrix} \longrightarrow \begin{matrix} CO_2 \\ NO \end{matrix} \xrightarrow{O_3} \begin{matrix} CO_2 \\ NO_2^* \end{matrix} \longrightarrow NO + h\nu$$

Scheme 51

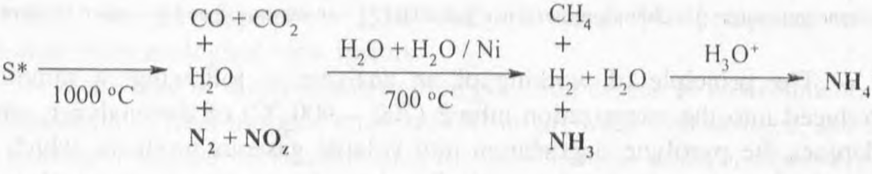
These gases are passed through the water trap 4 and are directed into the chemiluminescence's detector 6, where nitrogen oxides react with ozone with the formation of metastable nitrogen dioxide ($NO^*{}_2$). Return to the basic state of nitrogen dioxide causes a photoemission in the range of 650-900 millimicrons, which intensity is proportional to the nitrogen content in the analyzed sample (scheme 51).

4.2.2. Microcoulometric Titration System of Envirotech-Dohrmann, Model NCTS-10

Representative Micro-coulometric Titration System, produced by the Envirotech-Dohrmann Company [608], illustrates a principle of a coulometric determination of TON (Fig. 17). This instrument presents the example of fully automated acidimetric titration.

The principle of working of the analyzer is following: an analyzed sample is introduced via the auto-sampler 1 to the evaporation tube 3 (1100 °C) of the apparatus. The vaporized fraction in a stream of moist hydrogen is steered to the reduction tube 4 (700 °C), fulfilled with granulated nickel. In these conditions runs the quantitative conversion of bounded nitrogen to ammonia, which in the stream of hydrogen, is transferring successively into a cell of the microcoulometer 9, where it is subsequently titrated with coulometrically generated hydrogen ions.

The chemical reactions, being the basis of the analytic procedure applied (Fig. 17), are presented in scheme 52.



$$S^* \xrightarrow[1000\,^{\circ}C]{} \begin{matrix} CO + CO_2 \\ + \\ H_2O \\ + \\ N_2 + NO_z \end{matrix} \xrightarrow[700\,^{\circ}C]{H_2O + H_2O / Ni} \begin{matrix} CH_4 \\ + \\ H_2 + H_2O \\ + \\ NH_3 \end{matrix} \xrightarrow{H_3O^+} NH_4^+$$

Scheme 52

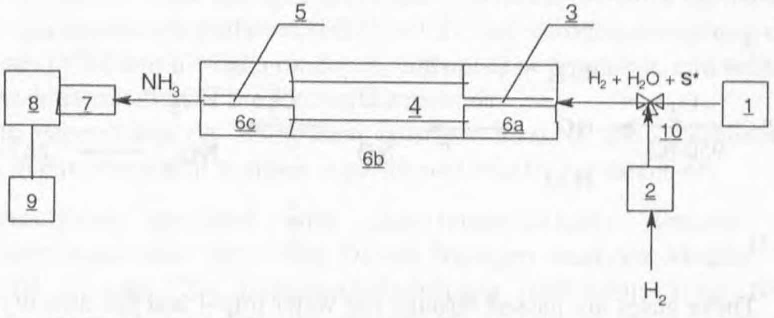


Fig. 17. Block diagram of an Envirotech-Dohrmann Microcoulometric Titration System Model NCTS-10 [608]:
1 – autosampler; 2 – humidizer; 3 – evaporation tube; 4 – hydrogenation tube, filled with granulated Ni; 5 – outlet of the reactor inlet (1100 °C); 6 – furnace with zone heating [6a (1100 °C), 6b (700 °C) and 6c (300 °C)]; 7 – thermostat (110 °C); 8 – acid-base titration cell; 9 – microcoulometer with digital readout; 10 – valve system; S* – sample.

4.2.3. The Analyzer of Nitrogen Constructed by Ventura

An interesting construction solution employing the conjunction of two combustion methods, namely the LTC (wet combustion of sample to NO$_z$) and the HTC (NO$_z$ → N$_2$) methods and the sequent final chromatographic determination of nitrogen using TCD, was elaborated by Ventura [381,421,422,443,444]. The ideological scheme of the nitrogen analyzer of Ventura is in Fig. 18 presented.

The principle of working of the analyzer is following: a sample (5-10 mg) is transferred to the degradative reactor 2, where in a solution of chromic and sulfuric acids undergoes to the oxidative degradation, forming a mixture of carbon monoxide and dioxide, water, nitrogen oxides and molecular nitrogen. The gas products of degradation ($CO + CO_2 + H_2O + NO_z + N_2$) are washed out from the reactor 2 by helium, and the formed gas mixture is passed through the oxidative-reductive column 3 (CuO–Cu).

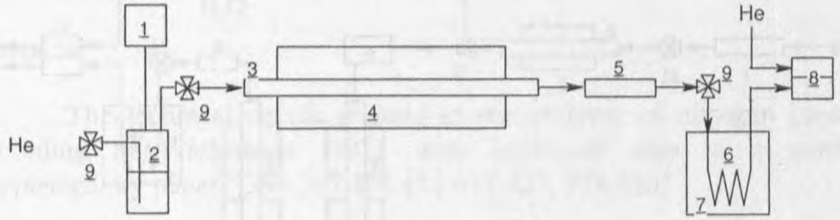
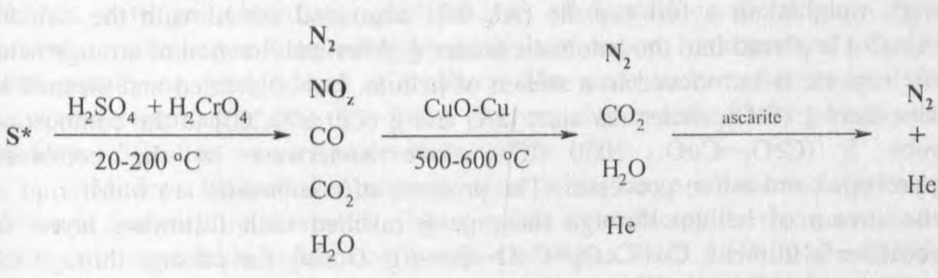


Fig. 18. Ideological scheme of nitrogen analyzer according to Ventura:
1 - feeder of samples; 2 - reactor for degradation wet-oxidative degradation ($H_2SO_4 + H_2CrO_4$); 3 - tube for catalytic reduction of nitrogen oxides; 4 - electric tubular oven (500-600 °C); 5 - dryer; 6 – chromatographic column; 7 - thermostat; 8 - TCD; 9 - system of valves and manometers.

Here at temperature 500-600 °C (CuO), carbon monoxide is quantitatively oxidized to dioxide, and on more far reductive layers (Cu) the reduction of nitrogen oxide to molecular nitrogen follows (scheme 53).



$$S^* \xrightarrow[20\text{-}200\,^{\circ}C]{H_2SO_4 + H_2CrO_4} \begin{matrix} N_2 \\ NO_z \\ CO \\ CO_2 \\ H_2O \end{matrix} \xrightarrow[500\text{-}600\,^{\circ}C]{CuO\text{-}Cu} \begin{matrix} N_2 \\ CO_2 \\ H_2O \\ He \end{matrix} \xrightarrow{\text{ascarite}} \begin{matrix} N_2 \\ + \\ He \end{matrix}$$

Scheme 53

A mixture of gas products in helium is initially dried in the absorber 5 (filled with anhydrone layer) and steered to the thermostated chromatographic column 6 (filled with Poropak) where it follows the isolation of nitrogen, determined in the TCD detector 8.

4.2.3. The Analyzer of Nitrogen Constructed by Waśkowski

In the alternative approach, Waśkowski [397,400,580] subjected samples to the HTC combustion by means of Co_3O_4 in a helium atmosphere. Nitrogen oxides during combustion formed, was subsequently reduced ($NO_z \rightarrow N_2$) in originally constructed reductive tube, then, after absorption of water and carbon dioxide in ascarite containing absorber, nitrogen was separated off chromatographically and determined using TCD. The ideological scheme of the analyzer of Waśkowski is in Fig. 19 presented.

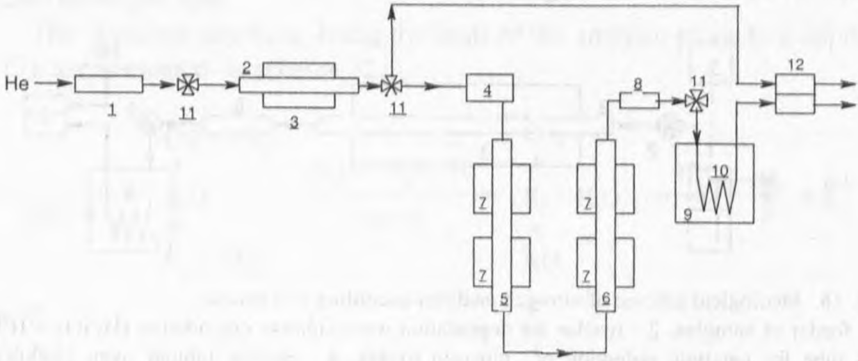
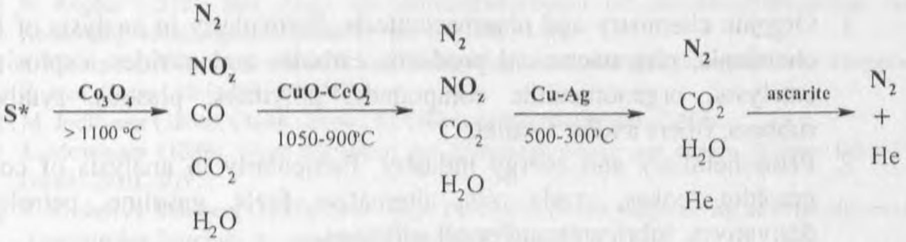


Fig. 19. Ideological scheme of nitrogen analyzer according to Waśkowski [397]:
1 – helium dryer; 2 – helium cleaner pipe; 3 – electric oven; 4 – samples feeder; 5 – combustion tube; 6 – reduction tube; 7 – electric tubular stoves; 8 – absorber with ascarite; 9 – thermostat; 10 – chromatographic column; 11 – systems of valves and manometers; 12 – TCD

The principle of working of an analyzer is following: a sample (0.3 to 4 mg), weighed in a foil capsule (Al, 0.01 mm) and mixed with the oxidant (Co_3O_4) is placed into the automatic feeder 4. After stabilization of arrangement, the capsule is introduced in a stream of helium, [initially dried and cleaned in absorbers 1 (SiO_2, molecular sieve 5A) and 2 (Cu; 600 °C)] to the combustion tube 5 (CeO_2–CuO; 1050 °C) where underwent to the combined pyrolysis/combustion processes. The products of combustion are transferred in the stream of helium through the pipe 6 fulfilled with following layers of reactive fulfillment: Cu–CeO_2–CuO–Cu–Ag. During the passage through the oxidative fulfillments [CuO (1050 °C)–CeO_2 (900 °C)–CuO (900 °C)] of the tube 6, the full conversion of formed initially volatile nitrogenous compounds to nitrogen oxides (NO_z) occurs. The sequential passage of the combustion gases through the reductive zone of fulfillment [CuO (800 °C)–Cu (500 °C)–Ag (200-300 °C)] is accompanied by the reduction of nitrogen oxides to molecular nitrogen ($NO_z \rightarrow N_2$). The gas mixture, goes out from the reductive tube 6 and containing the combustion derived components (CO_2, H_2O and N_2) is passed through the ascarite containing absorber 8 (removal of CO_2 and $H_2O_{(g)}$), is directed to chromatographic separation on the column 10, followed by the TCD detection (12). Scheme of the chemical transformations, taking place during analysis in the analyzer of Waśkowski, are on scheme 54 presented.



Scheme 54

The technical details relating to the analyzer of nitrogen constructed according to Waśkowski [397], were published also in a number of supplementary papers [396,397,406,414-417,423, 428,580].

5. Conclusions

The classical Pregl and Dumas methods for determination of carbon, hydrogen and nitrogen in organic substances involve tedious, time-consuming microanalytical techniques which require expensive, special laboratories and highly skilled technicians. Despite these shortcomings, they retain their usefulness and popularity because they provide accurate and reliable results.

The conjunction of high temperature combustion according to Pregl or Dumas, with gas chromatographic analysis of formed combustion products provides a simultaneous organic microanalysis of carbon, hydrogen and nitrogen with equally acceptable level of accuracy. The same instruments are used for oxygen determination according to the Unterzaucher modified method and with minor modification are used to determine sulfur.

Modern Elemental Analyzers offer wide range solutions supporting different analytical requirements. Conceived as a flexible platform, in which the basic unit is available in four configurations: CHN, CHNS, CHN-O and CHNS-O. The highly computerized analytical process provides the following areas of information:

1. The Molecular Identification data (CHN-O-S percentage; C/N, C/H area ratio; empirical formula);
2. The Heat Value (caloric values of fuels calculated on the basis of their MI data);

3. The CHN data Without Weighing (empirical formula calculations without weighing).

These Elemental Analyzers offer exceptionally wide range of application, illustrated here in the following areas.

1. Organic chemistry and pharmaceuticals. Particularly in analysis of fine chemicals, pharmaceutical products, carbides and nitrides, explosives, catalysts, organometallic compounds, polymers, plastics, synthetic rubbers, fibers and/or textiles.
2. Petrochemistry and energy industry. Particularly in analysis of coals, graphite, cokes, crude oils, alternative fuels, gasoline, petroleum derivatives, lubricants and/or oil additives.
3. Material characterization. In analysis of: papers, fibers, cement, ceramics, tyres, pigments, dyes and/or building materials.
4. Environmental sample analysis. Particularly in analysis of composts, wastes, sewage sludges, glass filters, fertilizers, pesticides, woods, soils, sediments.
5. Food industry sample. Analysis of: foods, nutrients, animal feed, proteins, tobacco, brewing, beverage.
6. Biological samples. Particularly in analysis of biological tissues, plants, algae, plankton, and so on.

The very simple instrument lay-out can be modified at any time, to accommodate the most diverse analytical application from stable Isotope Ratio Mass Spectrometry to CHNS-O determination of less than 10 mmg of pure organic substance, or for protein determination in food and feeds.

REFERENCES

[1] J. Gay-Lussac, L. Thenard (1811). Ann. Chim. (Paris), 79 (1811) 60; (cited in Ref. [386]).

[2] J. Gay-Lussac, L. Thenard (1815). Ann. Chim. (Paris), 95 (1815) 184; (cited in Ref. [386]).

[3] J.B. Dumas (1831). Ann. et Phys., 53 (1831) 198; (cited in Ref. [386]).

[4] J. Liebig (1831). *Uber eine neue Apparat zur Analyse organischen Korper und uber die Zusammensetzung einiger organischer Substanzen.* Pogg. Ann., 21 (1831) 1-25.

[5] J. Liebig (1837). *Arbeitung zur Analyze organischer Korper.* Braunschweig.

[6] H. Limpricht (1858). *Notiz uber Stickstoffhaltiger organischen Verbindunge.* Ann., 108 (1858) 46-50.

[7] L. Carius (1860). *Uber die Elementaranalyse organischer Verbindungen.* Ann., 116 (1860) 1-16.

[8] A. Kekule (1861). *Untersuchengen uber organische Saure.* Ann. Supplemententband **I**, **1861**, 340-384.

[9] L. Carius (1865). *Bestimmung von Schwefel, Chlor, Phosphor u.s.w. in organischen Substanzen.* Ann., 136 (1865) 129-141.

[10] J. Love (1870). Z. anal. Chem., 22 (1870) 217; (cited in Ref. [386]).

[11] J. Volhard (1877). *Die Annendung des Schwefelcyanammonium in der Massananalyse.* Annalen, 190 (1877) 1-61.

[12] F. Kopfer (1878). *Das Platin als Saurestoffubertrager bei der Alementaranalyse der Kohlenstofferbindungen.* Z. Anal. Chem., 17 (1878) 1-53.

[13] J. Kjeldahl (1883). *Neue Methode zur Bestimmung aus Stckstoffes in organischen Korpern.* Z. anal. Chem., 22 (1883) 366-382.

[14] M. Jodlbauer (1886). Chem,. Zentr., 57 (1886) 433; (cited in Ref. [386]).

[15] J. Messinger (1888). *Neue Methoden zur Elementaranalyse auf nassen Menge.* Ber., 21 (1888) 2910-2919.

[16] F. Kirster, A. Stallberg (1893). *Uber einige Derivative des Mesitilenes und die Verseifberkeit aromatischer Saurenitrile.* Annalen, 278 (1894) 207-223.

[17] S.M. Dennstedt (1897). *Vereinfachung der organischen Elementar-Analyse.* Ber., 30 (1897) 1590-1597.

[18] J.W. Gunning (1899). *Uber eine Modification der Kjeldahl Methode.* Z. anal. Chem., 28 (1899) 188-191.

[19] H. Baubigny, G. Chavanne (1903). Compt. Rend., 136 (1903) 1197; (cited in Ref. [396]).

[20] H. Pringsheim (1903). *Uber ein Schnellverfahren zur quantitativen Bestimmung von Chlor, Brom und Jod in organischen Verbindungen mit Natriumperoxyd.* Ber., 36 (1903) 4244-4246.

[21] F. Emich, J. Donau (1909). *Treatment of small amounts of precipitates. A contribution to qualitative and quantitative microchemical analysis.* Monatsh, 30 (1909) 745-747; CA: 4 (1910) 1002.

[22] J. Marek (1911). *Combustion tube for organic analysis.* J. Prakt. Chem., 84 (1911) 713-731; CA: 7 (1913) 2139.

[23] A. Kurtenacker (1911). *Contribution on ultimate analysis.* Z. anal. Chem., 50 (1911) 548-565.

[24] F. Pilch (1911). *Volumetric determination with small quantities of liquids.* Monatsh, 32 (1911) 21-29; CA: 5 (1911) 1570.

[25] F. Pregl (1912). *Abderhaldens Handbuch der biochemischen Arbeitsmethoden.* Abt. 5, Teil. II, Berlin, Vien, 1912.

[26] L.W. Winkler (1913). *Determination of small amounts of ammonia.* Z. angew. Chem., 26 (1913) 231-232.

[27] W.C. Cope (1916). *Kjeldahl modification for determination of nitrogen in nitro substitution compounds.* Ing. Eng. Chem., 8 (1916) 592-593.

[28] F. Pregl (1916). *Die quantitative organische Microanalyse*, Berlin, 1916.

[29] R.J. Cain, L.C. Maxwell (1919). *An electrolytic resistance method for determining carbon in steel.* J. Ind. Eng. Chem. Anal. Ed., 11 (1919) 852-860.

[30] H.H. Willard, W.E. Cake (1920). *The iodometric determination of amino nitrogen in organic substances.* J. Amer. Chem. Soc., 42 (1920) 2646-2650.

[31] J.K. Parnas, R. Wagnew (1921). *Determination of small amounts of nitrogen by the Kjeldahl method.* Biochem. Z., 125 (1921) 253-256; CA: 16 (1922) 942.

[32] J. Lindner (1922). *Volumetric determination of carbon and hydrogen in organic compounds.* Ber., 55 (1922) 2025-2031.

[33] H. ter Meulen (1922). *Determination of nitrogen in organic compounds.* Rec. Trav. Chim., 41 (1922) 121-123; CA: 19 (1925) 226.

[34] E. Muller, H. Barck (1923). *Decomposition of nitric oxide when heated with metals.* Z. anorg. allgem., 129 (1923) 309-320.

[35] J. Heslinga (1924). *New method for the determination of chlorine, bromine and iodine in organic compounds.* Rec. Trav. Chim., 43 (1924) 551-560.

[36] D.R. Nanji, W.S. Shaw (1924). *Application of "formol" titration in the Kjeldahl method of determination of nitrogen.* Analyst, 49 (1924) 558; CA: 19 (1925) 1110.

[37] D.D. Van Slyke, J.M. Neuli (1924). *Determination of gases in blood and other solutions by vacuum extraction and manometric measurement.* J. Biol. Chem., 61 (1924) 523-573; CA: 18 (1924) 3615.

[38] J. Lindner (1925). *Volumetric determination of carbon and hydrogen in elementary analysis.* Z. anal. Chem., 66 (1925) 305-307.

[39] E. Berl, H. Burckhardt (1926). *A rapid, semimicrochemical method of determining nitrogen.* Ber. 59 (1926) 897-900.

[40] A. Elek, H. Sobotka (1926). *Kjeldahl-Pregl method applied for nitro compounds.* J. Amer. Chem. Soc., 48 (1926) 501-503.

[41] B. Flaschentrager (1926). *Experiences in organic microanalysis* Z. anorg. Chem., 39 (1926) 717-722.

[42] M.M. Nicloux (1927). *Microdetermination of carbon. Applications.* Compt. Rend., 184 (1927) 890-891; CA: 21 (1927) 1945.

[43] B. Bobrański, E. Sucharda (1928). *Elementary centigram analysis. I. Determination of carbon and hydrogen with automatic regulation of combustion.* Roczn. Chem., 8 (1928) 290-323.

[44] A. Boivin (1928). *Application of the carbon microdetermination method of Nicloux to the determination of urea.* Bull. Soc. Chim. Biol., 10 (1928) 684-697; CA: 22 (1928) 3184.

[45] F. Halla (1929). *Carbon dioxide-carbon monoxide equilibrium over copper.* Z. anorg. allgem. Chem., 180 (1929) 83-88.

[46] F. Hernler (1929). *Elementary organic analysis by Pregl microchemical method.* Mikrochemie Pregl-Festschrift, **1929**, 140-153.

[47] M.F. Lauro (1931). *Use of selenium as catalyst in determination of nitrogen by the Kjeldahl method.* Ind. Eng. Chem. Anal. Ed., 3 (1931) 401-402; CA: 25 (1931) 5938.

[48] H. Lieb, H.G. Krainick (1931). *New microchemical determination of carbon by wet combustion.* Mikrochimie, 9 (1931) 367-384; CA: 25 (1931) 4187.

[49] J. Lindner (1931). *Determination of carbon and hydrogen. Progress in the volumetric determinations of carbon and hydrogen in the service of ultimate analysis.* Mikrochemie, 4 (1931) 321-328.

[50] J. Lindner (1931). *Experiences in the volumetric determination of water.* Z. anal. Chem., 86 (1931) 141-153.

[51] J.B. Niederl, J.R. Meadow (1931). *Organic ultra micro-analytical determination of carbon and hydrogen with a fraction of a milligram substance.* Mikrochemie, 9 (1931) 350-359; CA: 25 (1931) 4201.

[52] O.P. Trautz (1931). *The micro-Dumas method.* Mikrochemie, 3 (1931) 300-312.

[53] A. Friedrich (1932). *New technique for combustion in microchemical elementar analysis.* Angew. Chem., 45 (1932) 476-478.

[54] P.L. Kirk, P.A. Williams (1932). *Microdetermination of carbon. Improvements in the Nicloux method.* Ind. Eng. Chem. Anal. Ed., 4 (1932) 403-404; CA: 26 (1932) 5868.

[55] J.B. Niederl, B. Whitman (1932). *Microanalytical determination of carbon and hydrogen in an atmosphere of nitrogen.* Mikrochemie, 11 (1932) 274-300.

[56] E. Schadendorff, M.K. Zacherl (1932). *New micro-determination of carbon by wet combustion. II. Combustion of liquids.* Mikrochimie, 10 (1932) 99-108; CA: 26 (1932) 43.

[57] E.P. Clark (1933). *Semi-microdetermination of nitrogen by the Dumas method.* J. Assoc. Offic. Agr. Chem., 16 (1933) 575-580; CA: 28 (1934) 70.

[58] A. Friedrich, E. Kuhas, E. Schnurch (1933). *The general application of the micro-Kjeldahl determination.* Z. Physiol. Chem., 216 (1933) 68-76; CA: 27 (1933) 2648.

[59] A. Kapustinsky, L. Shamovsky (1933). *A method for the direct determination of the dissociation pressure of metallic oxides.* Z. anorg. allgem. Chem., 216 (1933) 10-16.

[60] W.R. Kirner (1934). *Direct simultaneous determination of carbon, hydrogen and oxygen in organic substances. I. Analysis of pure compounds containing carbon and hydrogen without halogens.* Ind. Eng. Chem. Anal. Ed., 6 (1934) 358-363.

[61] K. Fischer (1935). *A new method for the determination of the water content of liquids and solids.* Angew. Chem., 48 (1935) 394-396.

[62] W.R. Kirner (1935). *Direct simultaneous determination of carbon, hydrogen and nitrogen in organic substances. III. Analysis of pure compounds containing carbon, hydrogen and nitrogen.* Ind. Eng. Chem. Anal. Ed., 7 (1935) 366-368.

[63] I.M. Kolthoff, V.A. Stenger (1935). *Calcium hypochlorite as a volumetric oxidizing agent. Stability and standarization of the solution. Determination of ammonia.* Ind. Eng. Chem. Anal. Ed., 7 (1935) 79-81; CA: 29 (1935) 2876.

[64] J. Lindner (1936). *Supplement to the microdetermination of carbon and hydrogen. Volumetric determination of carbon dioxide.* Mikrochemie, 20 (1936) 209-224.

[65] R.T. Milner, M.S. Sherman (1936). *Organic microanalysis. I. Nitrogen by Dumas method.* Ind. End. Chem. Anal. Ed., 8 (1936) 331-332; CA: 30 (1936) 7490.

[66] D.F. Hayman, S. Adler (1937). *Microanalysis of nitrogen in certain pyrymidines by the Dumas method.* Ind. Eng. Chem. Anal. Ed., 9 (1937) 197.

[67] J. Milbauer (1937). *Relations of the substance to be oxidized to the effectiveness of catalyst. VII. Kjeldahl catalysts.* Chem. Obzor, 13 (1938) 25-35; CA: 31 (1937) 2077.

[68] E. Sucharda, Cz. Troszkiewicz (1938). *Determination of carbon and nitrogen In organic compounds.* Roczniki Chemii, 18 (1938) 784-797; CA: 33 (1939) 6197.

[69] H. Gysetl (1939). *The microchemical, gasometric determination of nitrogen in organic compounds.* Helv. Chim. Acta, 22 (1939) 1088-1095.

[70] G. Ingram (1939). *Semimicromethod for the determination of carbon and hydrogen in organic compounds.* J. Soc. Chem. Ind., 58 (1939) 34-37; CA: 33 (1939) 2845.

[71] J.B. Niederl, V. Niederl (1939). *Simplified combustion tube filling for micro-determination of carbon and hydrogen.* Mikrochemie ver Mikrochim. Acta, 26 (1939) 28-32.

[72] M. Schutze (1939). *New method for the direct determination of oxygen in organic substances.* Z. anal. Chem., 118 (1939) 251-255.

[73] D.H. Smith, W.M.D. Bryant, J. Mitchell (1939). *Analytical procedures employing Karl Fisher's reagent. I. Nature of the reagent.* J. Amer. Chem. Soc., 61 (1939) 2407-2412.

[74] A.E. Beet, R. Belcher (1940). *A rapid method for the simultaneous determination of sulphur and halogen in organic compounds.* Fuel, 19 (1940) 42-45; CA: 34 (1940) 4530.

[75] R. Belcher (1940). *Rapid method for the determination of carbon in coal.* Fuel, 19 (1940) 172-174; CA: 34 (1940) 7578.

[76] R. Belcher, C.E. Spooner (1940). *A rapid method for the ultimate analysis of coal.* Fuel, 20 (1941) 130-134; CA: 35 (1941) 8246.

[77] J. Cartiaux (1940). *Determination of organic nitrogen.* Ann. chim. anal. chim. appl., 22 (1940) 92; CA: 34 (1940) 4698.

[78] F. Fischer (1940). *The micro-determination of nitrogen according to Dumas-Pregl.* Chem. Fabrik, 13 (1940) 154-156; CA: 34 (1940) 5015.

[79] E.W.D. Huffman (1940). *Determination of sulfur in organic compounds. New microchemical method.* Ind. End. Chem. Anal. Ed., 12 (1940) 53-58; CA: 34 (1940) 962.

[80] A. Lacourt, Ch.T. Chang (1940). *Quantitative organic microanalysis. The micro-determination of nitrogen by hydrogenation.* Bull. soc. chim. Belg., 49 (1940) 167; CA: 36 (1942) 60.

[81] A.R. Ronzio (1940). *A semi-micro-Dumas method applied for difficult combustible compounds.* Ind. Eng. Chem. Anal. Ed., 12 (1940) 303-304.

[82] E.H. Titow (1940). *Quantitative organic elementary analysis. Determination of carbon and hydrogen.* Zawod. Lab., 9 (1940) 853-859; CA: 35 (1941) 1355.

[83] D.D. Van Slyke, I. Folch, J. Plazin (1940). *Manometric carbon determination.* J. Biol. Chem., 136 (1940) 509-541.

[84] F. Acree (1941). *Collaborative report on the micro and semimicro Kjeldahl nitrogen determination.* J. Assoc. Off. Agr. Chem., 24 (1941) 648-654; CA: 35 (1941) 7310.

[85] R. Belcher, A.L. Godbert (1941). *Semimicro-method for the determination of organic nitrogen.* J. Soc. Chem. Ind. (London), 55 (1941) 196-198; CA: 35 (1941) 7877.

[86] PJ Elving, WH. Mc Elroy (1941). *Removal of nitrogen oxides in the semimicro-determination of carbon and hydrogen.* Ind. Eng. Chem. Anal. Ed., 13 (1941) 660-663.

[87] E. Rauterberg, H. Benischke (1941). *Various methods for digestion of organic substances in the Kjeldahl nitrogen determination.* Bodenkunde und Pflanzenerahr, 26 (1941) 97-105; CA: 37 (1943) 3013.

[88] I. Sarudi (1941). *A rapid Kjeldahl nitrogen determination.* Untersuch. Lebensm., 32 (1941) 451; CA: 37 (1943) 2300.

[89] G. Ingram (1942). *Universal apparatus for micro- and semimicro-determination of carbon and hydrogen.* J. Soc. Chem. Ind. (London), 61 (1942) 112-115; CA: 37 (1943) 2223.

[90] T.S. Ma, G. Zuazaga (1942). *Micro-Kjeldahl determination of nitrogen. A new indicator and improved rapid method.* Ind. Eng. Chem. Anal. Ed., 14 (1942) 280-282; CA: 36 (1942) 2499.

[91] R. McCready, W.Z. Hassid (1942). *Semimicro-determination of carbon.* Ind. Eng. Chem. Anal. Ed., 14 (1942) 526.

[92] L.P. Pepkovitz, A.L. Prince, F.E. Bear (1942). *Rapid Kjeldahl digestion method using perchloric acid.* Ind. Eng. Chem. Anal. Ed., 14 (1942) 856; CA: 37 (1943) 580.

[93] L.P. Pepkovitz, J. Shive (1942). *Kjeldahl nitrogen determination: a rapid wet digestion method.* Ind. Eng. Chem. Anal. Ed., 14 (1942) 914; CA 37 (1943) 1098.

[94] W.H. Taylor, G.F. Smits (1942). *Micro Kjeldahl nitrogen determination without use of titration procedure.* Ind. Eng. Chem. Anal. Ed., 14 (1942) 437-439; CA: 36 (1942) 4054.

[95] A. Beatty (1943). *Anhydrous cupric sulphate in Kjeldahl nitrogen determination.* Ind. Eng. Chem. Anal. Ed., 15 (1943) 476; CA: 37 (1943) 4986.

[96] G. Ingram (1943). *Use of silver vanadate in microcombustion of organic compounds.* J. Soc. Chem. Ind. (London), 62 (1943) 175-176; CA: 38 (1944) 529.

[97] H. Leopold (1943). *Notes on the work of Imre Sarudi: on a quick method for Kjeldahl determination.* Z. Lebensm. Untersuch und Forsch., 86 (1943) 220-226; CA: 41 (1947) 7305.

[98] R.O. Clark, G.H. Stillson (1945). *Microdetermination of carbon and hydrogen.* Ind. Eng. Chem. Anal. Ed., 17 (1945) 520-522; CA: 39 (1945) 4562.

[99] H. Gonick, D.D. Tunnicliff, E.D. Peters, L. Lekken, V. Zahn (1945). *Determination of nitrogen by combustion. Improved Dumas apparatus and recycle procedure.* Anal. Chem., 17 (1945) 677-682.

[100] J.A. Kaye, N. Weiner (1945). *Semimicro Kjeldahl nitrogen determination.* Ind. Eng. Chem. Anal. Ed., 17 (1945) 397-398.

[101] R.L. Shirley, W.W. Becker (1945). *Determination of nitrogen in pyridine ring-type compounds by the Kjeldahl method.* Ind. Eng. Chem. Anal. Ed., 17 (1945) 437-438; CA: 39 (1945) 3756.

[102] J.D. Cole, C.R. Parks (1946). *Semimicro-Kjeldahl procedure for control laboratories.* Ind. Eng. Chem., Anal. Ed., 18 (1946) 61; CA: 40 (1946) 1408.

[103] K. Marcali, W. Rieman (1946). *Kjeldahl determination of nitrogen. Elimination of the distillation.* Ind. Eng. Chem. Anal. Ed., 18 (1946) 709; CA: 41 (1947) 514.

[104] D.D. Van Slyke, I. Folch (1946). *Manometric carbon determination.* J. Biol. Chem., 136 (1946) 509-514.

[105] R.O. Clark, G.H. Stillson (1947). *Automatic microdetermination of carbon and hydrogen.* Anal. Chem., 19 (1947) 423-426.

[106] A.E. Heron (1947). *Oxidation of nitrogen during the microcombustion of organic compounds.* Analyst, 72 (1947) 142-149.

[107] W. Kirsten (1947). *Apparatus for micro- and semimicro-determination of nitrogen according Dumas.* Anal. Chem., 19 (1947) 925-927.

[108] G. Ingram (1948). *Critical examination of the empty-tube combustion method.* Analyst, 73 (1948) 548-551.

[109] A. Lindebaum, J. Schubert, W.D. Amstrong (1948). *Rapid wet combustion method for carbon determination with particular reference to isotopic carbon.* Anal. Chem., 20 (1948) 1120-1121.

[110] K. Marcali, W. Rieman (1948). *Kjeldahl determination of nitrogen without distillation. Application to samples containing phosphorus.* Anal. Chem., 20 (1948) 381-382.

[111] C.L. Ogg, R.W. Brand, C.O. Willits (1948). *Micro and semimicro-determination of nitrogen in heterocyclic compounds by a Kjeldahl method.* J. Assoc. Off. Agr. Chemists, 31 (1948) 663-669; CA: 43 (1949) 7373.

[112] H.M. Rauen, M. Buchka (1948). *Microdetermination of nitrogen by a Kjeldahl method.* Angew. Chem., 60 (1948) 209-210.

[113] A. Bennett (1949). *Use of reduced copper in the microdetermination of carbon and hydrogen.* Analyst, 74 (1949) 188-189.

[114] L.M. Brancone, W. Fulmor (1949). *Determination of nitrogen in difficult combustible ring compounds. Modification of the micro-Dumas procedure.* Anal. Chem., 21 (1949) 1147-1150.

[115] P.S. Ferrington, C. Nieman, H.E. Swift (1949). *Determination of carbon by wet combustion.* Anal. Chem., 21 (1949) 1423-1424.

[116] J. Grodsky (1949). *Microdetermination of chlorine and bromine.* Anal. Chem., 21 (1949) 1551-1553.

[117] J.K. Parnas (1949). *Determination of nitrogen by Kjeldahl method.* Zh. Anal. Khim, 4 (1949) 54-59.

[118] G.L. Stragand, H.W. Safford (1949). *Microdetermination of sulfur in organic compounds. A simplified gravimetric method.* Anal. Chem., 21 (1949) 625-628.

[119] R. Belcher, R. Ingram (1950). *Rapid microcombustion method for determination of carbon and hydrogen.* Anal. Chem. Acta, 4 (1950) 118-129.

[120] W.E. Gelman, M.O. Korszun (1950). *Microanalytical determination of nitrogen by hydrogenation.* DAN AN SSSR, 72 (1950) 895-898.

[121] G. Kainz (1950). *Determination of carbon and hydrogen.* Mikrochemie ver. Mikrochim. Acta, 35 (1950) 569-571; CA: 45 (1951) 6534.

[122] P.L. Kirk (1950). *Kjeldahl method for total nitrogen.* Anal. Chem., 22 (1950) 354-358.

[123] W. Kirsten (1950). *Dumas nitrogen determination using nickel oxide.* Anal. Chem., 22 (1950) 358-360.

[124] W. Kirsten (1950). *Micro and semimicro-determination of carbon and hydrogen.* Mikrochemie ver. Mikrochim. Acta, 35 (1950) 217-235.

[125] A. Lewin, B.G. Oberholzer, T.P. Whitehead (1950). *The micro-Kjeldahl determination of serum proteins, with selenium and copper as catalysts. Interrelation of the time and digestion and constituents of the digestion mixture.* Analyst, 75 (1950) 561-563.

[126] R.M. Silverstein, R. Perthel (1950). *Kjeldahl microdetermination.* Anal. Chem., 22 (1950) 949-950.

[127] J. Unterzaucher (1950). *Microchemical determination of nitrogen by the Dumas method as modified by Unterzaucher.* Chem. Ing. Technik, **22** (1950) 39-40; CA: 44 (1950) 3840.

[128] C.O. Willits, C.L. Ogg (1950). *Report on standardization of microchemical methods; micro-Kjeldahl nitrogen determination.* J. Assoc. Office Agr. Chemists, 33 (1950) 179-188.

[129] A. Dirscherl, W. Padowetz, W. Wagner (1951). *Determination of nitrogen.* Mikrochemie ver. Mikrochim. Acta, 38 (1951) 271-2; CA: 45 (1951) 9421.

[130] G.R. Lake, Ph. Mac Cutchan, R. Van Meter, J.C. Neel (1951). *Effects of digestion temperature on Kjeldahl analyses.* Anal. Chem., 23 (1951) 1634-1638.

[131] P.D. Sternglanz, R.G. Thompson, W.L. Savell (1951). *Dumas microdeter-mination of nitrogen in refractory organic compounds.* Anal. Chem., **23** (1951) 1027-1030.

[132] J. Unterzaucher (1951). *Elementary determination of oxygen, a method of determining carbon and hydrogen developed from it, and a new procedure for carring out the Dumas nitrogen determination for compounds difficult to burn.* Microchemie ver. Microchim. Acta, 36/37 (1951) 706-726.

[133] J.C. Van Meter, C.W. Bailey, E.C. Brodie (1951). *Evaluation of Dumas procedures by Mass Spectrometry. Determination of nitrogen in shake oil petroleum.* Anal. Chem., 23 (1951) 1638-1639.

[134] D.D. Van Slyke, J.P. Plazin, JR Weisiger (1951). *Reagents for the Van Slyke-Folch wet carbon combustion.* J. Biol. Chem., 191 (1951) 299-304.

[135] D.D. Van Slyke, R. Stelle, J. Plazin (1951). *Determination of total carbon and its radioactivity.* J. Biol. Chem., 191 (1951) 769-805.

[136] W.C. Alford (1952). *Microdetermination of nitrogen in organic compounds.* Anal. Chem., 24 (1952) 881; CA: 46 (1952) 7935.

[137] V.B. Fish (1952). *Hydrazones, semicarbazones, and other nitrogeneous substances requiring a reductive pretreatment. A semi-Kjeldahl procedure.* Anal. Chem., 24 (1952) 760-762.

[138] H. Gysel (1952). *Semiautomatic, micro-gasometric rapid determination of nitrogen in organic compounds.* Helv. Chim. Acta., 35 (1952) 802-807.

[139] G. Kainz (1952). *A new procedure for the gravimetric determination of carbon and hydrogen.* Mikrochemie ver. Mikrochim. Acta, 39 (1952) 166-175.

[140] W. Kirsten (1952). *Micro and semimicro Kjeldahl distillation apparatus.* Anal. Chem., 24 (1952) 1078.

[141] W. Kirsten (1952). *Dumas determination of nitrogen.* Mikrochemie ver. Mikrochim. Acta, 35 (1952) 245-246; CA: 46 (1952) 9347.

[142] W. Kirsten, J. Alperowicz (1952). *Micro- and semimicro-determination of halogens.* Mikrochemie ver. Mikrochim. Acta, 39 (1952) 234; CA: 46(1952) 9467.

[143] G.R. Lake (1952). *Determination of nitrogen in petroleum and shake oil.* Anal. Chem., 24 (1952) 1806-1811.

[144] R. Levy (1952). *Quantitative microanalysis.* Bull. Soc. Chim. Fr., (**1952**) 728; CA: 46 (1952) 11038.

[145] Ph. Mc Cutchan, W.F. Roth (1952). *Determination of nitrogen. Modified Kjeldahl procedure using thiosalicylic acid.* Anal. Chem., 24 (1952) 369-370.

[146] C.L. Ogg, C.O. Willits (1952). *Report on microanalytical determination of nitrogen for hydrazine-, nitroso- and nitro- linkages.* J. Assoc. Offic. Agr. Chem., 35 (1952) 288-291; CA: 46 (1952) 11034.

[147] L.P. Pepkowitz (1952). *Micro-determination of azide by Kjeldahl procedure.* Anal. Chem., 24 (1952) 900-901.

[148] W.H. Trockmorton, G.H. Hutton (1952). *Use of magnesium oxide in determination of carbon and hydrogen in fluoro-organic compounds.* Anal. Chem., 24 (1952) 2003-2004.

[149] N.E. Gelman, M.O. Korshun (1953). *A new method of simultaneous microdetermination of carbon and hydrogen in organic compounds.* DAN AN SSSR, 89 (1953) 685-687.

[150] G. Ingram (1953). *Microdetermination of nitrogen in organic compounds by the rapid combustion process.* Mikrochim. Acta, (**1953**) 137-141.

[151] W. Kirsten (1953). *Recent developments in quantitative organic microanalysis.* Anal. Chem., 25 (1953) 74-86.

[152] T. Mitsui (1953). *Organic elementary analysis. VI. Dissociation of carbon dioxide in contact with copper oxide and reduced copper and a modified combustion method for microdetermination of nitrogen.* Japan Anal., 2 (1953) 117-121; CA: 9 (1953) 7949.

[153] C.H. Perrin (1953). *Rapid modified procedure for determination of Kjeldahl nitrogen.* Anal. Chem., 25 (1953) 968-971.

[154] R.B. Bradstreet (1954). *Determination of nitro nitrogen by Kjeldahl method.* Anal. Chem., 26 (1954) 235-236.

[155] W. Mauser, A. Egli (1954). *New modificated method for nitrogen micro-determination by Unterzacher.* Helv. Chim. Acta, 37 (1954) 1048-1054.

[156] M. Vecera (1954). *Microdetermination of sulphur in organic compounds.* Chem. Listy, 48 (1954) 613-616.

[157] C.S. Adams, G.H. Spaulding (1955). *Determination of organic nitrogen by Kjeldahl method without distillation.* Anal. Chem., 27 (1955) 1003-1004.

[158] R. Belcher, J.E. Fildes, A.M.G. McDonald (1955). *The application of the Volhard method in semi-micro quantitative organic analysis.* Chem. & Industry, **1955**, 1402-1404; CA: 50 (1955) 2369.

[159] G. Kainz, F. Scholer (1955). *Microchemical determination of carbon and hydrogen with nickel as reducing agent fior nitrogen oxides.* Z. anal. Chem., 148 (1955) 6-9.

[160] I. Korbl (1955). *Analytical application of silver permanganate. I. Properties of silver permanagnate and the products of its thermal decomposition.* Chem. Listy, 49 (1955) 858-861.

[161] I. Korbl (1955). *Analytical application of silver permanganate. II. Properties of silver permanagnate and the products of its thermal decomposition.* Chem. Listy, 49 (1955) 862-866.

[162] I. Korbl (1955). *Catalyst for oxidative reactions.* Czech. Pat. 85.465 (1955); AA: 4 (1957) 2631.

[163] W. Schoniger (1955). *A micro-determination of nitrogen by decomposition with magnesium.* Microchim. Acta, **1955**, 44-48.

[164] W. Schoniger (1955). *A rapid micro-analytical determination of nitrogen in organic substances.* Microchim. Acta, **1955**, 123-124.

[165] R. Belcher, M.K. Bhatty (1956). *The reduction of nitro groups in organic compounds before digestion by Kjeldahl's method.* Analyst, 81 (1956) 124-125.

[166] R. Belcher, M.K. Bhatty (1956). *Elimination of distillation procedure in the Kjeldahl method.* Mikrochim. Acta, **1956**, 1183-1186.

[167] B. Bobrański (1956). *A new automatic apparatus for determination of ten-milligrams quantities of carbon, hydrogen and nitrogen in organic compounds.* Mikrochim. Acta, **1956**, 1735-1746.

[168] M. Fukuda (1956). *Organic elementar analysis. II. Determination of nitrogen in refractory compounds by modified micro-Dumas method.* J. Pharm. Soc. Jap., 76 (1956) 1041-1044; AA: 4 (1957) 2222.

[169] K. Hozumi, S.J. Kinoshita (1956). *Organic micro-analysis. XII. The rate of generation of oxygen from several metal oxides used for the combustion of the sample in the Dumas nitrogen determination.* J. Pharm. Soc. Japan, 76 (1956) 1157-1160; AA: 4 (1957) 2993.

[170] K. Hozumi, S.J. Kinoshita (1956). *Organic micro-analysis. XIII. Modification of the apparatus for the Dumas nitrogen determinations with a flow-checking device before the combustion tube with cobaltic oxide as oxidation agent.* J. Pharm. Soc. Japan, 76 (1956) 1161-1166; AA: 4 (1957) 2993.

[171] K. Hozumi, S.J. Kinoshita (1956). *Organic micro-analysis. XIV. An improved method for burning the sample by the use of cobaltic oxide as a source of oxygen in the Dumas nitrogen determination.* J. Pharm. Soc. Japan, 76 (1956) 1167-1169; AA: 4 (1957) 2993.

[172] G. Kainz, A. Resch, F. Scholler (1956). *Use of copper in the micro-determination of carbon and hydrogen.* Mikrochim. Acta., **1956**, 850-853.

[173] I. Korbl (1956). *Application of the thermal decomposition products of silver permanganate in organic analysis.* Mikrochim. Acta, **1956**, 1705-1721.

[174] R.N. McCoy, E.L. Bastin (1956). *Determination of carbon and hydrogen in organic fluorine compounds. Microcombustion method for gases, liquids and solids.* Anal. Chem., 28 (1956) 1776-1780.

[175] A. Okac, M. Vrchlabsky (1956). *Korbl method of catalytic combustion of organic compounds.* Chem. Listy, 50 (1956) 2042-2043.

[176] W. Schoniger (1956). *The rapid micro-analytical determination of halogens and sulfur in organic compounds.* Mikrochim. Acta, **1956**, 869-876.

[177] W. Schoniger (1956). *Progress report on quantitative organic microanalysis.* Microchim. Acta, **1956**, 1456-1466.

[178] R.B. Bradstreet (1957). *Acid requirement of the Kjeldahl digestion.* Anal. Chem., 29 (1957) 944-946.

[179] W. Kirsten (1957). *Dumas micro-determination of nitrogen.* Anal. Chem., 29 (1957) 1084-1089.

[180] T.S. Ma, R.E. Lang, J.G. McKinley (1957). *Determination of non-aminoid nitrogen by the micro-Kjeldahl method. I. Aromatic nitro compounds.* Mikrochim. Acta, **1957**, 368-377.

[181] L. Mazor (1957). *Carbon, hydrogen and fluorine determination in organic compounds.* Mikrochim. Acta, **1957**, 113.

[182] F.L. Schaffer, J.C. Sprecher (1957). *Routine determination of nitrogen in the microgram range with sealed tube digestion and direct nesslerization.* Anal. Chem., 29 (1957) 437-438.

[183] W. Schoniger (1957). *Method for the simultaneous determination of CHN content of organic compounds, by the use of a single sample.* Microchim. Acta, **1957**, 545-552.

[184] L. Synek, M. Vecera (1957). *Organic quantitative analysis. XI. Application of tricobalt tetraoxide as combustion catalyst in elementary analysis.* Chem. Listy, 51 (1957) 1551-1553.

[185] M. Vecera, L. Synek (1957). *Organic quantitative analysis. XVIII. Micro-determination of carbon and hydrogen using tricobalt tetraoxide as oxidation catalyst.* Chem. Listy, 51 (1957) 2266-2274.

[186] J.A. Kuck (1958). *Perspectives in quantitative organic microdeterminations.* Anal. Chem., 30 (1958) 1552-1556.

[187] M. Vecera, D. Snobl, L. Synek (1958). *Quantitative organic analysis. XIII. A rapid method for micro-determination of carbon and hydrogen in organic material.* Mikrochim. Acta, **1958**, 9-27.

[188] K. Hozumi, S. Amako (1959). *Organic microanalysis. XX. Modified Dumas nitrogen determination. The correct temperature for reduced layer of copper.* Mikrochim. Acta, **1959**, 230-242; CA: 54 (1960) 22171.

[189] F.A. Keidel (1959). *Determination of water in elementary analysis; by direct amperometric measurement.* Anal. Chem., 31 (1959) 2043-2048.

[190] A.S. Meyer, C.M. Boyd (1959). *Determination of water by titration with coulometric generated Karl Fischer reagent.* Anal. Chem., 31 (1959) 215-219.

[191] B. Schulek, K. Burger, M. Feher (1959). *Can the acid-containing receiver in the Kjeldahl distillation be replaced by one charged with boiled water?* Z. anal. Chem., 167 (1959) 28-31.

[192] W. Schoniger (1959). *Progress report on quantitative organic elementary micro-analysis.* Mikrochim. Acta, **1959**, 670-692.

[193] B. Stehr (1959). *Carbon and hydrogen microdetermination by automatic combustion control.* Anal. Chem., 31 (1959) 1274-1278.

[194] M. Vecera, L. Synek (1959). *Organic quantitative analysis. XXI. New method for the nitrogen determination with tricobalt tetraoxide as combustion catalyst.* Collect. Czech. Chem. Commun., 24 (1959) 3401-3406.

[195] H.C. Burk (1960). *Colorimetric micro-Kjeldahl method with direct nesslerization for routine determination of nitrogen.* Mikrochim. Acta, **1960**, 208-219.

[196] B. Cacace, R. Cipollini, G. Perez (1960). *Continuous elemental analysis of organic compounds in gas chromatographic effluents.* Science, 132 (1960) 1253-1254.

[197] N.E. Gelman, W. Wen-Jun (1960). *Conductometric micro-determintion of carbon and hydrogen in organic compounds.* Zh. Anal. Khim., 15 (1960) 487-494.

[198] S. Greenfield (1960). *A conductometric micro method for determining carbon in organic compounds.* Analyst, 85 (1960) 486-492.

[199] A. Kainz, H. Horvatisch (1960). *Oxidizing efficiency of mixed catalysts in the determination of carbon and hydrogen.* Z. anal. Chem., 177 (1960) 344-352.

[200] W. Struck (1960). *Rapid microdetermination of carbon in organic substances.* Mikrochim Acta, **1960**, 421-428.

[201] O.E. Sundberg, Ch. Maresh (1960). *Application of gas chromatography to microdetermination of carbon and hydrogen.* Anal. Chem., 32 (1960) 274-277.

[202] A.M. Vogl, J.J. Quattrone (1960). *Rapid gas chromatographic method for determination of carbon and hydrogen.* Anal. Chem., 32 (1960) 1754-1757.

[203] P.R. Woods (1960). *Rapid microanalytical method for determining carbon and hydrogen in fluoro-organic compounds.* Analyst, 85 (1960) 764-766.

[204] M. Ashraf, M.K. Bhatty, R.A. Shah (1961). *Determination of nitrogen in organic compounds by Kjeldahl method without distillation.* Anal. Chim. Acta, 25 (1961) 448-452.

[205] A. Gotz, H. Bober (1961). *Rapid determination of oxygen in organic substances.* Z. anal. Chem., 181 (1961) 92; CAN: **55**, 23164; AN: **1961**, 23164.

[206] C. Ingram (1961). *The combustion of organic compounds by ignition in oxygen: determination of carbon and hydrogen.* Analyst, 86 (1961) 411-414.

[207] E.C. Olson, R.L. Houtman, W.A. Struck (1961). *Rapid methods of elemental analysis. III. Precise coulometric determination of hydrogen in organic compounds.* Microchem. J., 5 (1961) 611-616.

[208] R.H. Reitsema, N.J. Allphin (1961). *Determination of nitrogen with gas chromatography.* Anal. Chem., 33 (1961) 355-359.

[209] F. Salzer (1961). *An automatic rapid micro-combustion apparatus for the determination of carbon and hydrogen in organic samples.* Z. anal. Chem., 181 (1961) 59-76.

[210] W. Walisch (1961). *Rapid ultramicro method for simultaneous determination of carbon, hydrogen and nitrogen in organic compounds.* Ber., 94 (1961) 2314-2327.

[211] D.R. Beurman, C.E. Meloan (1962). *Determination of sulphur in organic compounds.* Anal. Chem., 34 (1962) 319-322.

[212] M..H. Hashmi, E. Ali, M. Umar (1962). *Kjeldahl determination of nitrogen without distillation.* Anal. Chem., 34 (1962) 988-990.

[213] G. Kainz, H. Horwatisch (1962). *The different effects of oxide and metal catalyst in carbon-hydrogen and nitrogen analysis.* Mikrochim. Acta, **1962**, 7-15.

[214] G. Kainz, H. Horwatisch (1962). *Procedures for carbon-hydrogen and nitrogen determination. Influence of vaporization technique on the oxidative efficiency of the tube packing.* Z. anal. Chem., 187 (1962) 87-96.

[215] G. Kainz, J. Mayer (1962). *Lead dioxide – compound forvery efficient absorption of nitrogen dioxide in carbon and hydrogen analysis.* Z. anal. Chem., 191 (1962) 30-40.

[216] J.A. Kuck, J.W. Berry, A.J. Andreatch, P.A. Lentz (1962). *Microdeter-mination of carbon and hydrogen using nondispersive infrared and thermal conductivity detectors.* Anal. Chem., 34 (1962) 403-407.

[217] C.F. Nightingale, J.M. Walker (1962). *Simultaneous determination of carbon-hydrogen-nitrogen by gas chromatography.* Anal. Chem., 34 (1962) 1435-3147.

[218] W. Simon, P.F. Sommer, G.H. Lyssy (1962). *A complete automation of the microdetermination of carbon and hydrogen in organic compounds.* Microchem. J., 6 (1962) 239-258.

[219] P.F. Sommer, W. Sauter, J.T. Clerc, W. Simon (1962). *Self-integrating method for the rapid determination of carbon and hydrogen in organic compounds in milligram and submilligram amounts with use of katharometers.* Helv. Chim. Acta, 45 (1962) 595-600.

[220] M. Vecera (1962). *Quantitative organic analysis. XXXIII. Rapid semi-automatic micro-determination of nitrogen in organic substances, with tricobalt tetyraoxide as oxidative catalyst.* Mikrochim. Acta, 1962, 896-912.

[221] J.T. Clerc, W. Simon (1963). *Limitations of a self-integrating method for the simultaneous carbon, hydrogen and nitrogen determinations by thermal conductivity measurement.* Microchem. J., 7 (1963) 422-436.

[222] J.T. Clerc, R. Dohner, W. Sauter, W. Simon (1963). *A fully automatic installation for simultaneous determination of carbon, hydrogen and nitrogen on milligram and submilligram samples of organic compounds using a self-integrating thermal conductivity method.* Helv. Chim. Acta, 46 (1963) 2369-2388.

[223] W.N. Czumaszenko, P.E. Pachomova (1963). *Gasometric determination of nitrogen in organic compounds. 2. Formation of nitrogen oxide during pyrolytic decomposition.* Izv. AN SSSR, Ser. Khim., **1963**, 2090-2095.

[224] C.E. Van Hall, J. Safranko, V.A. Stenger (1963). *Rapid combustion method for the determination of organic substances in aqueous solutions.* Anal. Chem., 35 (1963) 315-319.

[225] G. Kainz, J. Mayer (1963). *Absorption of nitrogen oxides during CH-determinations. Use of lead dioxide for internal absorption.* Mikrochim. Acta, **1963**, 481-494.

[226] G. Kainz, J. Mayer (1963). *Absorption of nitrogen oxides during CH-determinations. The retention of carbon dioxide.* Mikrochim. Acta, **1963**, 542-551.

[227] G. Kainz, J. Mayer (1963). *Retention behavior of lead dioxide in carbon-hydrogen analysis.* Mikrochim. Acta, **1963**, 601-614.

[228] A. Lakomy, L. Lehar, M. Vecera (1963). *Quantitative organic analysis. XXXV. Microdetermination of carbon in organic substanes.* Collect. Czech. Chem. Commun., 28 (1963) 3271-3277.

[229] M.L. Parsons, S.M. Pennigton, J.M. Walker (1963). *A rapid combustion method for nitrogen determination utilizing gas chromatography.* Anal. Chem., 35 (1963) 842-844.

[230] C.H. Perrin (1963). *Rapid modified procedure for determination of Kjeldahl nitrogen.* Anal. Chem., 25 (1963) 968-971.

[231] A.P. Tierientiev, A.N. Turkerltaub, A.A. Bondarevskaya, L.A. Domokhina (1963). *Gas chromatographic determination of nitrogen and oxygen in organic compounds.* DAN AN SSSR, 148 (1963) 1316-1319.

[232] H. Trutnovsky (1963). *Rapid method for nitrogen determination.* Z. anal. Chem., 198 (1963) 331-334.

[233] D.C. White (1963). *Titrimetric determination of carbon in aqueous solutions and in organic compounds.* Talanta, 10 (1963) 727-736.

[234] J. Binkowski, B. Bobrański (1964). *Range of application of the van Slyke method for the determination of carbon in organic compounds.* Chem. Anal (Warsaw), 9 (1964) 515-526.

[235] J.M. Hibbs, G.H. Nation (1964). *Application of an electrolytic hygrometer to the determination of oxide in lead.* Analyst, 89 (1964) 49-54.

[236] M.J. Francis, E.J. Minnick (1964). *A modified Ingram-type combustion apparatus.* Mikrochem. J., 8 (1964) 245-256.

[237] G. Kainz, F. Scheidl (1964). *Use of platinum for carbon and hydrogen determination.* Mikrochim. Acta, **1964**, 196-200; CA: 12 (1964) 5841.

[238] G. Kainz, H. Scheidl (1964). *Combustion of organic compounds by the "empty tube" technique.* Z. anal. Chem., 202 (1964) 251-258..

[239] W.J. Kirsten (1964). *Micro-determination of carbon and hydrogen.* Mikrochim. Acta, **1964**, 487-507.

[240] H. Malissa, W. Schmidts (1964). *Relative conductometric determination of carbon, hydrogen, oxygen and sulfur in organic compounds.* Mikrochem. J., 8 (1964) 180-193.

[241] C.D. Miller, J.D. Winerfordner (1964). *An efficient instrumental procedure for the rapid determination of carbon and hydrogen in the submilligram range, and its extension to the determination of nitrogen.* Microchem. J., 8 (1964) 334-348.

[242] F. Salzer (1964). *Rapid combustion apparatus for electrical end-point indication for the determination of carbon and hydrogen in organic substances.* Z. anal. Chem., 205 (1964) 66-80.

[243] M. Vecera (1964). *Use of tricobalt tetraoxide for the destructive oxidation of organic materials.* Mikrochim. Acta, **1964**, 196-201.

[244] J.F. Alicino (1965). *Use of verniculite in carbon and hydrogen determination.* Microchem. J., 9 (1965) 22-25.

[245] J. Binkowski, M. Vecera (1965). *Organic quantitative analysis. XLI. Micro-determination of carbon and hydrogen in organophosphorus compounds.* Mikrochim. Acta, **1965**, 842-851; CA: 64 (1966) 18291.

[246] R.B. Bradstreet (1965). *The Kjeldahl method for organic nitrogen,* Academic Press, New York, London.

[247] P.J. Durrant, B. Durrant (1965). *Outlines of modern inorganic chemistry.* PWN, Warsaw, 1965.

[248] T. Flynn, O. Gruenke, A. Savitzky (1965). *Gas Chromatography Applications.* Nr. GC-AP-006, Perkin Elmer Corp., 1965.

[249] G.J. Kakabadse, B. Mahonin (1965). *Cerium (IV) oxide in carbon and hydrogen determinations.* Mikrochim. Acta, **1965**, 1136-1141.

[250] I. Monar (1965). *Simple, generally applicable micro-determination for the determination of carbon-hydrogen, nitrogen and oxygen, and an automatically controlled combustion apparatus developed for this purpose.* Mikrochim. Anal. Acta, **1965**, 208-250.

[251] M. Vecera, J. Lakomy, L. Lehar (1965). *Organic quantitative analysis. XL. Conductometric micro- and ultra-micro determination of carbon.* Mikrochim. Acta, **1965**, 674-678.

[252] F.A.J. Armstrong, P.M. Williams, J.D.H. Strickland (1966). *Photo-oxidation of organic matter in seawater by ultra-violet radiation: application.* Nature, 211 (1966) 481-482.

[253] A.R.D. Condon (1966). *A new automatic organic elemental micro-analyzer.* Microchem. J., 10 (1966) 408-426.

[254] G.H. Gustin, M.L. Teft (1966). *Improved accuracy of rapid micro-determination of carbon and hydrogen method of modified combustion-absorption technique.* Microchem. J., 10 (1966) 236-243.

[255] A.L. Lebiedieva, N.A. Nikolajeva, W.A. Orestova (1962). *On the micro-determination of carbon and hydrogen in fluoroorganic compounds.* Zh. Anal. Khim., 17 (1962) 993-997.

[256] C.D. Miller (1966). *A new high speed analyzer for the accurate submicrodeter-mination of carbon and hydrogen.* Microchem. J., 11 (1966) 366-375.

[257] N. Pechanec, J. Horacek (1966). *Determination of carbon and hydrogen in organic materials. Absorption of halogens and sulfur.* Mikrochim. Acta, **1966**, 357-369.

[258] E. Pell, L. Machherndl, H. Malissa (1966). *Recent results in relative conductometric elementary microanalysis.* Microchem. J, 10 (1966) 286-300.

[259] A.N. Prezioso (1966). *Performance of a new automatic organic microanalyzer.* Microchem. J., 10 (1966) 516-521.

[260] F. Salzer (1966). *Application of range of rapid combustion apparatus with electric indication for the determination of carbon and hydrogen.* Microchem. J., 10 (1966) 27-45.

[261] V. Svojanovsky, M. Krejci, K. Tesarik, J. Janak (1966). *Trace analysis by means of gas chromatography.* Chromatogr. Rev., 8 (1966) 90-171.

[262] M.L. Tefft, G.H. Gustin (1966). *Improved combustion techniques for the microdetermination of nitrogen in organic compounds with an automatic analyzer.* Microchem. J., 10 (1966) 175-183.

[263] W. Walisch, G. Scheuerbrandt, W. Marks (1966). *Additional techniques for submicro CHN-analysis: extension of sample range, combustion of liquids and hygroscopic compounds.* Microchem. J., 10 (1966) 3116-3122.

[264] P. Borda, L.D. Hayward (1967). *Nitrogen analysis of nitrate esters by micro-Dumas combustion.* Anal. Chem., 39 (1967) 548-552.

[265] A.A. Duswalt, W.W. Brandt (1967). *Carbon-hydrogen determination by gas chromatography.* Anal. Chem., 32 (1967) 272-274.

[266] F. Ehrenberger (1967). *Determination of nitrogen in organic substances by combustion in oxygen.* Z. anal. Chem., 228 (1967) 106-110.

[267] F. Ehrenberger, O. Weber (1967). *Organic elementary analysis in the micro-gram range. Determination of CHNO with the CHN-O ultra automatic analyzer.* Glas Instrum.-Tech., 11 (1967) 502-504; CAN: **68**, 56418; AN: **1968**, 56418.

[268] G. Kainz, K. Zidek (1967). *Absorption of nitrogen dioxide at 20 °C during determination of carbon and hydrogen. Comparison of various absorbents.* Mikrochim. Acta, **1967**, 7-16.

[269] K.F. Luft, G. Kesseler, K.H. Zorner (1967). *Non dispersive, infrared gas analysis, with the UNOR.* Chem. Ing. Technik, 39 (1967) 637-645; CA: 39 (1968) 101484.

[270] F.M.W. Olds, J.W. Patrick, F.H. Saw (1967). *Determination of sulfur in carbone and cokes by gas chromatography.* Analyst, 92 (1967) 54-56.

[271] S. Pemington, C.E. Meloan (1967). *Determination of nitrogen, carbon and sulfur in liquid compounds by gas chromatography.* Anal. Chem., 39 (1967) 119-121.

[272] W.G. Bieriezkin, B.M. Łuskina, S.W. Sjaweillo, A.P. Tierientiewa (1968). *A gas chromatographic method for determination of carbon and hydrogen in organic compounds.* Zh. Anal. Khim., 23 (1968) 1254-1257.

[273] R. Culmo (1968). *Micro-determination of oxygen in organic compounds with an automatic elementary analyzer.* Mikrochim. Acta, **1968**, 811-815.

[274] M..N. Czumaszenko, I.E. Pachanowa (1968). *A method of decomposition of organic compounds and simultaneous CHN determination by means of gas chromatography.* Izw. AN SSSR, Ser. Khim., (**1968**) 235-239.

[275] F. Kasler (1968). *Magnesium oxide as combustion-tube filling for the micro-analysis of phosphorus cotaining compounds.* Microchem. J., 13 (1968) 430-432.

[276] D.M. Knight, K. Inone (1968). *Nitrogen analysis of cinhophen derivatives on the Coleman analyzer.* Microchem. J., 13 (1968) 87-90.

[277] W. Merz (1968). *A rapid automatic method for nitrogen determination.* Z. anal. Chem., 237 (1968) 272-279.

[278] E. Pella (1968). *Use of hellium as carrier gas in the microdetermination of oxygen in organic substances.* Mikrochim. Acta, **1968,** 13-22.

[279] F. Scheidl (1968). *Oxygen donor for the F and M CHN-analyzer.* Microchem. J., 13 (1968) 155-157.

[280] W. Walisch, K. Schaefer (1968). *Combustion of F-, P-, and metal-containing compounds in an automatic CHN analyzer.* Mikrochim. Acta, **1968**, 765-772.

[281] R. Culmo (1969). *Automated micro-determination of carbon, hydrogen and nitrogen: improved combustion train and handling techniques.* Mikrochim. Acta, **1969,** 175-180.

[282] G. Dugan, V.A. Alvise (1969). *An analyzer for the dynamic micro-determination of carbon, hydrogen, nitrogen, oxygen and sulfur.* Anal. Chem., 41 (1969) 495-501.

[283] D.C. Gordon (1969). *Examination of methods of particulate organic carbon analysis.* Deep-Sea Res. Oceanogr. Abstr., 16 (1969) 661-665; CAN: **73**, 28703; AN: **1970**, 428703.

[284] N.E. Gelman, Z.M. Anashina (1969). *Quantitative analysis of metalloorganic compounds. Use of lead oxide in microdetermination of carbon, hydrogen and heteroelements in difficult combustible compounds.* Zh. Anal. Khim., 24 (1969) 1722-1726.

[285] M. Kan, Y. Tsukumoto, H. Kashiwagi, H. Kamio (1969). *Examination and modification of the automatic carbon, hydrogen and nitrogen analyzer.* Takeda Kenkyusho Nempo, 28 (1969) 40-49; CAN: **72**, 74545; AN: **1970**, 74545.

[286] W. Kisielew, J.I. Jaszin (1969). *Adsorptive gas chromatography.* PWN, Warsaw, 1969.

[287] W.A. Klimova, P.N. Dubinski (1969). *Formation of oxides of nitrogen during the determination of carbon and hydrogen by flash combustion of aromatic nitro-compounds in a stream of oxygen.* Izv. AN SSSR, Ser. Khim., **1969**, 191-196.

[288] W. Merz (1969). *Automated rapid micro-determination of carbon and hydrogen.* Anal. Chim. Acta, 48 (1969) 380-390.

[289] W. Padawetz (1969). *Comparative studies on combustion-tube fillings for the absorption of halogens and sulfur in carbon and hydrogen determination.* Microchem. J., 14 (1969) 110-125.

[290] M. Pechanec (1969). *Determination of carbon and hydrogen in organic compounds. VI. Factors influencing the formation of nitrogen dioxide during the catalytic oxidation of nitrogen containing compounds.* Collect. Czech. Chem. Commun., 34 (1969) 3455-3470.

[291] E. Pella (1969). *Experiences and trends in organic microanalysis.* Corsi Chim., **1969**, 53-57; CA: 72 (1970) 28207.

[292] E. Pella (1969). *Removal of oxides of nitrogen by oxido-reduction in the micro-determination of carbon and hydrogen.* Microchim. Acta, **1969,** 490-503.

[293] F. Scheidl (1969). *Experiences with some oxygen donors being used for CHN analysis in the decimiligram and ultramiligram range.* Fresenius' Z. Anal. Chem, 245 (1969) 30-32.

[294] J.W Wimberley (1969). *Rapid method for the analysis of total and organic carbon in shale with a high-frequency combustion furnace.* Anal. Chim. Acta,, 48 (1969) 419-422.

[295] W. Diudorf, H. Hocker (1970). *Comparative analysis of variance of the Kjeldahl nitrogen and a neutron activation nitrogen technique* (in Ger.). Z. anal. Chem., 250 (1970) 29-33; AA: 20 (1971) 4380.

[296] W.H. Doty, A.W. Munson, D.E. Wood, E.L. Schneider (1970). *Comparative analysis of variance of the Kjeldahl nitrogen and a neutron-activation nitrogen technique.* J. Ass. Analyt. Chem, 58 (1970) 801-803; AA: 20 (1971) 4380.

[297] G. Ege (1970). Tables in mass spectrometry and elementary analysis; determination of CHNO(S) molecular formulas. (Zahlentafeln zur Massenspektrometrie und Elementaranalyse; Ermitltung von CHNO(S)-Summenformeln). **1970**, Verlag Chemie, Weinheim; CAN: **73**, 71264; AN: **1970**, 471264.

[298] A. Henriksen (1970). *Determination of total nitrogen, phosphorus and iron in fresh water by photo-oxidation with ultra-violet radiation.* Analyst, 95 (1970) 601-608.

[299] W. Merz (1970). *New automatic unit for the micro-determination of nitrogen in various samples.* GIT Fachz.-Lab., 14 (1970) 617-622; AA: 20 (1970) 3879.

[300] K. Ono, K. Nakamura, M. Yamamuro, K. Kawada (1970). *Microanalysis. IX. Automation of F & M CHN analyzer,* Sankyo Kenkyusho Nempo, 22 (1970) 34-40; CAN: **74**, 134761; AN: **1971**, 134761.

[301] K. Ono, M. Yamamuro, K. Kawada (1970). *Microanalysis. XI. Test of a CHN analyzer by a nonweighing method.* Sankyo Kenkyusho Nempo, 22 (1970) 49-53; CAN: **74**, 134759; AN: **1971**, 134759.

[302] M. Pechanec (1970). *Determination of carbon and hydrogen in organic compounds. VIII. Suppression of nitrogen dioxide in the catalytic combustion of organic nitrogen-containing*

compounds, and the effect of nitrogen dioxide in the determination of hydrogen. Collect. Czech. Chem. Commun., 35 (1970) 3793-3799.

[303] M. Pechanec, J. Horacek (1970). *CDetermination of carbon and hydrogen in organic compounds. VII. Factors that affect the catalytic efficiency for the cobalt (II/III) oxides obtained by thermal decomposition of Co(II) oxalate.* Collect. Czech. Chem. Commun., 35 (1970) 2749-2759.

[304] V. Rezl (1970). *Simultaneous determinations of carbon, hydrogen and nitrogen by means of gas chromatography.* Microchem. J., 15 (1970) 381-390.

[305] M. Shimimizu, K. Hozumi (1970). *Statistical analysis of analytical precision of the automated C-H-N analyzer with a differential thermal conductivity detector.* Bunseki Kagaku, 19 (1970) 1041-1049; AN: **1970**, 526688.

[306] R.M. Silverstein, G.C. Bassler (1970). *Spectroscopic methods in organic compounds identification.* PWN, Warsaw, 1970.

[307] A. Bielicka (1971). *Determination of carbon, hydrogen and nitrogen by the use of a CHN 185 (HP) analyzer.* Petrochemia, 11 (1971) 107-111.

[308] J. Binkowski (1971). *Determination of carbon and hydrogen by a rapid micro-gravimetric metod.* Mikrochim. Acta, **1971**, 892-898.

[309] P. Foster, A.W. Morris (1971). *Seasenal variation of dissolved ionic and organically associated copper in Menai Streets.* Deep-Sea Res., 18 (1971) 231-236; CA: 75 (1971) 25077.

[310] D. Fraisse (1971). *Determination of carbon in organic compounds by combustion and automated coulometric titration of carbon dioxide.* Talanta, 18 (1971) 1011-1015.

[311] W.J. Kirsten (1971). *Ultramicrodetermination of CHN with a modified Walisch-Technicon analyzer.* Microchem. J., 16 (1971) 610-625.

[312] S.S. Kriwołapow, E.S. Rusajew, A.A. Antonow (1971). *Apparatus for elemental analysis by reaction-gas chromatography.* Zawodskaja Łab., 37 (1971) 142; CA: 74 (1971) 119856.

[313] W. Merz (1971). *Completely automatic apparatus for oxygen determination with use of a table computer.* Mikrochim. Acta, **1971**, 71-80.

[314] W. Merz (1971). *Fully automated method for the determination of oxygen in organic substances with colorimetric end-point indication.* Anal. Chim. Acta, 53 (1971) 429-435.

[315] L. Synek, M. Vecera, V. Kratochvil (1971). *A general method for determination of carbon and hydrogen in organic compounds containing fluor, phosphorus and silicon heteroatoms.* Collect. Czech. Chem. Commun., 36 (1971) 2606-2614.

[316] W.C. Urban (1971). *Modification of the Kjeldahl nitrogen determination method.* Anal. Chem., 43 (1971) 800-801.

[317] E. Wachberer, A. Dirscherl, K. Pulver (1971). *Automatic procedure for the CHN-analysis of organic substances in the milligram range.* Microchem. J., 16 (1971) 318-328.

[318] B. Wojciechowska (1971). *Determination of carbon and hydrogen in products of carbon hydrogenation by gas chromatography.* Chem. Anal. (Warsaw), 16 (1971) 135-141.

[319] A. Colombo, R. Vivian (1972). *Application of an automatic organic element analyzer to the determination of CHN in inorganic compounds.* EUROATOM Rep. No 5060 (1972) 375; CAN: **80**, 10003; AN: 1974, 10003.

[320] B.T. Croll (1972). *Determination of organic carbon in water.* Chem. Ind. (London), **1972**, 386.

[321] R.F. Culmo (1972). *Micro-determination of sulfur with an automatic analyzer.* Microchem. J., 17 (1972) 499-507.

[322] S. Ebel (1972). *Automated and computer-controlled system in micro elemental analysis for the simultaneous CHN determination.* Fresenius' Z. Anal. Chem., 262 (1972) 349-352.

[323] N.E. Gelmn, N.J. Larina, J.S. Czekaszewa (1972). *Quantitative analysis of organo-element compounds. Use of lead oxide for microdetermination of nitrogen by Dumas in difficulty combustible compounds.* Zh. Anal. Khim., 27 (1972) 612-616.

[324] K. Nakamura, K. Ono Kikushige, K. Katsuke (1972). *Gas chromatographic – coulometric determination of carbon and hydrogen in organic compounds.* Mikrochem. J., 17 (1972) 338-346.

[325] C.I. Kennedy (1972). *Technique for automatic CHN determination of volatile liquid sample.* Microchem. J., 17 (1972) 325-326.

[326] E. Kozłowski, B. Kobylińska-Mazurek, M. Biziuk (1972). *Determination of carbon and nitrogen by ignition mineralization method.* Chem. Anal. (Warsaw), 17 (1972) 109-119.

[327] A.J. Libiediewa, N.A. Nikołajewa, W.A. Orestowa (1972). *On the micro-determination of carbon and hydrogen in fluoroorganic compounds.* Zh. Anal. Khim., 17 (1972) 993-997.

[328] F.T. Lindgren, G.R. Stevens, L.C. Jensen (1972). *Elemental carbon, hydrogen and nitrogen microanalysis of crushed rock and soil samples.* J. Amer. Oil Chem. Soc., 49 (1972) 208-214; CAN: **76**, 156815; AN: **1972**, 156815.

[329] W. Merz (1972). *Modern rapid methods of elementary analysis (for CHNO) involving the use of an electronic computer.* Bull. Soc. Chim. Fr., **1972**, 2521-2532.

[330] W. Merz, E. Brodkorb, M. Kranz (1972). *Electronic data processing applied for organic elementary analysis.* Mikrochim. Acta, **1972**, 939-954.

[331] I. Monar (1972). *Automatic apparatus for the simultaneous micro-determina-tion of carbon, hydrogen and nitrogen.* Mikrochim. Acta, **1972**, 784-806.

[332] K. Nakamura, K. Ono, K. Kawada (1972). *Coulometric determination of carbon and hydrogen in organic compounds.* Mikrochemie, 17 (1972) 338-346; AA: 25 (1973) 1607.

[333] K. Ono, M.A. Kashiwagi, T. Takahashi, S. Oochi, E. Enomoto, K. Kawada (1972). *Microanalysis. XIII. Improvement of the reduction train in the F&M HP CHN analyzer.* Sankyo Kenkyusho Nempo, 24 (1972) 73-7; CAN: **78**, 154599; AN: **1973**, 154599.

[334] C.E. Schupp (1972). *Gas chromatography.* PWN, Warsaw, 1972.

[335] R. Stoffel (1972). *Automatic CHNO microelemental analysis of 23 samples with a new analyzer; an electronic balance and a small computer.* Mikrochim. Acta, **1972**, 242-246.

[336] Y. Takahashi, R.T. Moore, R.J. Joyce (1972). *Direct determination of organic carbon in water by reductive pyrolysis.* Int. Lab., **1972**, 21-28; AA: 25 (1973) 1299.

[337] W. Thurauf, H. Assesenmacher (1972). *Rapid determination of carbon and hydrogen in organic compounds by non-dispersing infra-red absorption.* Z. anal. Chem., 262 (1972) 263-266.

[338] A. Colombo, R. Vivian (1973). *Determination of CHN in inorganic compounds by means of an automatic organic elemental analyzer.* Microchem. J., 18 (1973) 589-595.

[339] F. Ehrenberger, S. Gorbach (1973). *The methods of organic elemantar and trace analysis. [Methoden der organischen Elemental and Spurenanalyze.]* Verlag Chemie Gmbh, Weinheim, 1973.

[340] G.M. Gustin (1973). *Automation in microchemistry: automate carbon-hydrogen-nitrogen analyzer case history.* Progr. Anal. Chem., **1973**, 5319-5326; CAN: **81**, 468603; AN: **1974**, 468603.

[341] E. Haeberli (1973). *Automated elementary analysis without weighing of the sample, and computer calculation of molecular formulas.* Mikrochim. Acta, **1973**, 597-603.

[342] E. Kozłowski, M. Biziuk (1973). *Comparison of binding ability of phosphorus by reagents applied in elementary analysis. Reliable method of carbon and hydrogen determination in phosphorus containing compounds.* Chem. Anal. (Warsaw), 18 (1973) 341-349.

[343] E. Kozłowski, B. Kobylińska-Mazurek (1973). *A reliable method for determining carbon and hydrogen in phosphorus containing organic compounds.* Chem. Anal. (Warsaw), 18 (1973) 1161-1168.

[344] G.M. Maciak, R.A. Byers, P.W. Landis (1973). *Computerized technique in organic microelemental analysis: determination of CHN-O.* Microchem. J., 18 (1973) 8-17.

[345] E. Pella, B. Colombo (1973). *Study of carbon, hydrogen and nitrogen determi-nation by combustion-gas chromatography.* Mikrochim. Acta, **1973,** 697-719.

[346] Y. Tomida, T. Ando, W. Funasaka (1973). *Micro-determination of carbon and hydrogen in organic fluorine compounds by the sodium fluoride method.* Japan Analyst, 22, 1465 (1973) 1465-1469; AA: 28 (1975) 3C4.

[347] K. Ubik (1973). *Automation in organic analysis. III. Micro- and ultramicro determination of nitrogen.* Microchem. J., 18 (1973) 19-29.

[348] J.M. Baldwin, R.E. McAtee (1974). *Determination of organic carbon in water with a silver-catalyzed peroxydisulphate wet-chemical oxidation method.* Microchem. J., 19 (1974) 179-190.

[349] M. Ellison (1974). *Aids and modifications carried out to a Crlo Erba CHN analyzer.* Chem. Ind. (London), **1974**, 787-788.

[350] K. Hakariya, H. Sato, T. Akehata (1974). *Data processing on elemental analysis.* Bull. Tokyo Inst. Technol. 122 (1974) 23-26; CAN: **83**, 525808; AN: **1975**, 525808.

[351] R. Karlson (1974). *Coulometric microdetermination of carbon and nitrogen in organic compounds.* Mikrochim. Acta, **1974**, 963-972.

[352] E. Kozłowski (1974). *Simple apparatus for carbon and hydrogen determination by mineralization in air current.* Chem. Anal. (Warsaw), 19 (1974) 835-842.

[353] J. Małyszko (1974). *Operation multipliers and their application in instrumental analysis. I. Fundamentals and basic systems.* Chem. Anal. (Warsaw), 19 (1974) 243-256.

[354] F.G. Romer, J.W. van Shaik, K. Baunt, B. Griepink (1974). *Automated determination of carbon and hydrogen. VII. Determination of carbon and hydrogen in organic samples in the range 0.2 to 2 milligrams.* Z. anal. Chem., 272 (1974) 97-101.

[355] G. Telek, N. Marshall (1974). *Using a CHN analyzer to reduce carbonate interference in particulate organic carbon analyses.* Mar. Biol., 24 (1974) 219-121; CAN: **81**, 416592; AN: **1974**, 416592.

[356] H. Trutnovsky (1974). *A novel combustion system for the micro-determination of nitrogen.* Microchem. J., 19 (1974) 347-352.

[357] P. Volfel, H. Sontheimetr (1974). *New method of determination of organic carbon in water by photo-oxidation.* Vom Wasser, 43 (1974) 315-325.

[358] P.D. Goulden, P. Brooksbank (1975). *Automated determinations of dissolved organic carbon in lake water.* Anal. Chem., 47 (1975) 1943-1946.

[359] D. Grosjean (1975). *Solvent extraction and organic-carbon determination in atmosphere particulate matter. Extraction organic carbon analyzer technique.* Anal. Chem., 47 (1975) 797-805.

[360] V. Rezl, B. Kaplanowa (1975). *Apparatus for elemental microanalysis of organic substances by frontal chromatography.* Mikrochim. Acta, **1975 I**, 493-503.

[361] R.E. Salo, W.L. Oaks, R.D. McPhee (1975). *Measuring the organic carbon content of source emission for air pollution control.* J. Air Pollut. Control Assoc., 25 (1975) 390-393; CA: 82 (1975) 174665.

[362] H. Weitkamp (1975). *Developments in the CHN-O analyses*. Method. Chem., **1975**, 1 Pt. A 178-183, Publ. Academic, New York; CAN: **83**, 157506; AN: **1975**, 557506.

[363] Cooperative work (1975). *Detection and quantitative interpretation of experimental data in gas chromatography*. Ossolineum, Kraków, 1975.

[364] J. Binkowski, S. Giziński, R. Kamiński, W. Reimschusel (1976). *Study of the behavior of P-oxides in the combustion of phosphorus-bearing organic compounds and their absorption on suitable substances by means of compounds labeled with* ^{32}P. Mikrochim. Acta, **1976 I**, 623-641.

[365] V.P. Grigoryan, B.D. Ryzhkov, L.V. Kostina (1976). *Characteristics of the CHN-185 analyzer for the analysis of organic compounds*. Zavod. Lab., 42 (1976) 926-927; AA: 32 (1977) 3C2.

[366] F. Nydhal (1976). *On the optimum conditions for the reduction of nitrate to nitrite by cadmium*. Talanta, 23 (1976) 349-357.

[367] A.D. Semenov, B.G. Soyer, W.A. Bryzgalo, L.S. Kosmenko (1976). *Photochemical mineralization of organic substances in determination of carbon, phosphorus and nitrogen in natural waters*. Zh. Anal. Khim., 31 (1976) 2030-2037.

[368] Z. Suprynowicz (1976). *Modern trends in chromatographic theory and practice*. Ossolineum, Wrocław, 1976.

[369] J. Binkowski, S. Giziński, (1977). *Investigations of absorption of the phosphorus oxides arising in the combustion of organophosphorus compounds by means of* ^{32}P*-labelled substances*. Mikrochim. Acta, **1977 II**, 487-494.

[370] F. Bodart (1977). *Elemental analysis of fertilizers by fast-neutron activation*. J. Radioanal. Chem., 38 (1977) 241-246.

[371] L.S. Chuang, D.A. Miller, W.P. Lay, W.Y. Chin (1977). *The 14-MeV-neutron activation analysis of Chinese foodstuffs for protein content*. J. Radioanal. Chem., 38 (1977) 279-289.

[372] D. Fraisse, N. Schmitt (1977). *Automatic microanalyzers. III. Automatic analyzer for rapid microdetermination of nitrogen*. Microchem. J., 22 (1977) 109-130.

[373] G. Giovannini, G. Poggio, S. Carvelli (1977). *Determination of soil nitrogen: comparison between two automated techniques*. Agric. Ital., 77 (1977) 19-24; CAN: 90 (1977) 37953.

[374] R.A. Srapenyants, I.P. Saveliev (1977). *Multi-element analysis of plants and fertilizers*. J. Radioanal. Chem., 38 (1977) 247-255.

[375] Supelco-Inc. (1977). *The analysis of gases and light hydrocarbons by gas chromatography*. Supelco, Bellefonte, PA (1977).

[376] W.J. Becker (1978). Process analyzer for determination of total organic carbon. GIT Fachz. Lab., 22 (1978) 386-391.

[377] R. Bertoni (1978). Automatic determination of CN in suspended matter of natural water with Carlo Erba 1106 CHN elemental analyzer. MIIMAS 36 (1978) 297-301; CAN 92 (1980) 152745.

[378] S.C. Byers, E.L. Mills, P.L. Stewart (1978). *A comparison of methods of determination organic carbon in marine sediments, with suggestion from standard methods*. Hydrobiology, 58 (1978) 43-47; AN: **1978**, 464981.

[379] Carlo Erba (1978). *Short Notes - elemental organic microanalysis yesterday and today*. C. Erba, Milano, 1978.

[380] J.W. Kirsten (1978). *Micro and trace determination of oxygen in organic compounds*. Anal. Chim. Acta, 100 (1978) 279-288.

[381] K. Komarek, K. Ventura, Z. Smrecek, J. Churacek, J. Janak (1978). *Application of frontal technique in reaction gas chromatography for the determination of hydrazine and its derivatives*. Collect. Czech. Chem. Commun., 43 (1978) 1863-1866.

[382] J.H. Lowry, K.H. Mancy (1978). *Rapid automated system for analysis of dissolved total organic nitrogen in aqueous solutions.* Water Res., 12 (1978) 471-474; AA: 37 (1979) 3H 53.

[383] V. Rezl (1978). *Automatic carbon, hydrogen, nitrogen and oxygen elemental analysis without weighing.* Mikrochim. Acta, **1978/I**, 493-506.

[384] W.J. Becker (1979). *Determination of total organic carbon in waste water.* GWF-Gas, Wasserfach: Wasser/Abwasser, 120 (1979) 217-229; AA: 39 (1980) 2H 48.

[385] B. Bobrański (1979). *Quantitative analysis of organic compounds.* Warsaw, **1979**, PWN.

[386] V.P. Grigorian, T.V. Platonowa (1979). *Features of the use of model CHN-185B analyzer.* Zavod. Lab., 45 (1979) 889-891; CAN: **92**, 3387; AN: **1980**, 33387.

[387] E. Kozłowski, J. Namieśnik (1979). *Determination of total carbon and total organic carbon from volatile air pollutants. V. Determination of total carbon and total organic carbon in laboratory air.* Mikrochim. Acta, **1979 I**, 345-352.

[388] K. Ono, T. Takahashi, E. Enomoto, M. Tamaru (1979). *Studies on microanalysis. XXII. Further improvement of the auto-sampler for F&M CHN analyzer.* Sankyo Kenkyusho Nempo, 31 (1979) 65-72; CAN: 92 (1980) 211117.

[389] R.A. Van Steenderen, W.D. Basson, F.A. van Duuren (1979). *Automated chemical analysis for measuring levels of organic carbon in potable waters.* Water Res., 13 (1979) 539-543; AA: 39 (1980) 5H 53.

[390] S. Allie, R. Ranoiouix (1980). *Stack sampling of organic compounds: application to the measurement of catalytic incinerator efficiency.* J. Air Pollut. Control Assoc., 30 (1980) 792-794; CA: 95 (1980) 11916

[391] K. Danzer, E. Than, D. Molch (1980). *Analysis – determination of substance contents.* WNT, Warsaw, 1980.

[392] S. Giziński (1980). *Investigations on the absorption of phosphorus oxides in combustion tube during carbon and hydrogen determination by combustion-analysis of organophosphorus compounds.* Ph. D. Dissertation Book, Center of Molecular and Macromolecular Studies. Polish Academy of Sciences, Łódź, Poland.

[393] L.M. Kiparenko, N.E. Gelman, N.D. Masternikova, V.I. Smirnova, (1980). *Automatic CHN analysis of organic and metaloorganic compounds.* Zh. Anal. Khim., 35 (1980) 328-334.

[394] M. Malaiyandi, M.H. Sadar, P. Lee, R. O'Grady (1980). *Removal of organics in water using hydrogen peroxide in presence of ultraviolet light.* Water Res., 14 (1980) 1131-1132; CA: 93 (1980) 225442.

[395] R.A. Van Steenderen, J.S. Lin (1981). *The measurement of total organic carbon and total organohalogens as parameters for water quality evaluation.* Anal. Chem., 53 (1981) 2157-2160.

[396] B. Waśkowski (1981). *Juncture unit.* Author cert. Nr. 44622/ 33694.

[397] B. Waśkowski, R. Gondko (1981). *Determination of nitrogen in decigram scale.* Chem. Anal. (Warsaw), 26 (1981) 599-603.

[398] A. Zgirski, R. Gondko (1981). *Biochemical calculations.* Warsaw, PWN, **1981**.

[399] J. Jankowski (1982). *Balances and high precision weighing.* WNT, Warsaw, 1982.

[400] B. Waśkowski, R. Gondko (1982). *Chromatographic adapter for elementary analysis in ultramicro scale.* Chem. Anal. (Warsaw), 27 (1982) 183-190

[401] Varian (1982). *Varian AG CDS-111 Chromatography Data System. Varian Ed.*, Basel, 1982.

[402] Waters Associates. (1982). *Poropak – Gas Chromatography – Column Packing Material.* Waters, 1982.

[403] ZOCH (1982). *Polichrom A - Informative proposal.* ZOCH, Lublin, 1982.

[404] P. Blazka, L. Prochazkova (1983). *Mineralisation of organic matter in ultra-violet by radiation.* Water Res., 17 (1983) 355; AA: 46 (1984) 3H 55.

[405] I. Holdermann, S. Bessel (1983). *History of instrumental analysis. Part IV. Micro-elemental analysis (CHN).* Chem. Labor. Betr. 34 (1983) 459-460.

[406] R. Gondko, B. Waśkowski (1983). *Rapid – automated determination of nitrogen in biological samples by gas chromatography.* Diagn. Lab., XIX (1983) 1-3.

[407] A. Otsuki, Y. Ino, T. Fujii, (1983). *Simultaneous measurements ad determinations of stable carbon and nitrogen isotope ratios, and organic carbon and nitrogen contents in biological samples by coupling of a small quadrupolle mass spectrometer and modified CN elemental analyzer.* Int. J. Mass Spectrom. Ion Phys. 48 (1983) 343-346. CAN: **98**, 122388; AN: **1983**, 122388.

[408] V. Rezl, J. Uhdehova (1983). *Elemental analysis of CHN in liquid samples with the CHN-1 analyzer without weighing.* Ropa Uhlie, 25 (1983) 678-684; CAN: **100**, 95807; AN: **1984**, 95807.

[409] H. Sandorfy-Bozsoky (1983). *Determination of oxygen content of phosphorus-containing compounds.* Nehezvegyip. Kut. Intez. Kopzl., 14 (1983) 159-164; CAN: **100**, 169811; AN: **1984**, 169811.

[410] J. Binkowski (1984). Automated determination of carbon, hydrogen and nitrogen in organic compounds Chem. Anal. (Warsaw), 29 (1984) 1-17.

[411] L. Gustafsson (1984). Interference's in the determination of total nitrogen in natural waters by photo-oxidation of nitrate-nitrite mixture. Talanta, 31 (1984) 979-986.

[412] V. Rezl, J. Uhdehova (1984). *Determination of CHNO in liquid samples of organic substances using the CHN-1 analyzer without weighing,* Zh. Anal. Khim., 39 (1984) 2210-2216.

[413] J.I. Hedges, J.H. Stern (1984). *Carbon and hydrogen determination of carbonate-containing solids.* Limnol. Oceanogr., 19 (1984) 657-663; CAN: **101**, 162788; CAN: 101, 562788; AN: **1984**, 562788.

[414] B. Waśkowski (1984). *Automated sample adapter.* Pat. PRL Nr. 119777 (1983).

[415] B. Waśkowski (1984). *Procedure for preparation of pyrolytic tube for elementary analysis in ultra-micro scale based on thermal conductivity.* Pat. PRL Nr. 124 992. (1984).

[416] B. Waśkowski (1984). *Procedure for ultramicro scale elementary analysis.* Pat. PRL Nr. 126 339 (1984).

[417] B. Waśkowski, R. Gondko (1984). *Automated sample adapter.* Pat. PRL Nr. 123683 (1984).

[418] G.B. Howe, R.K.M. Jaynaty, J.E. Knoll, M.R. Madgett (1985). *EPA reference method 25. Laboratory evaluation and field testing.* J. Air Pollut. Control Assoc., 35 (1985) 735-739; CA: 103 (1985) 182851.

[419] R.A. Nadkarmi, R.B. Cornett, R.L. Bredeweg (1985). *Evaluation of an elemental analyzer.* Am. Lab., 17 (1985) 72-81; CAN: **102**, 116292; AN: **1985**, 116292..

[420] R. Rohl, H.J. Hoffman (1985). Quantification of carbon dioxide in water by inductively coupled plasma atomic emission spectroscopy. Fresenius' Z. Anal. Chem., 322 (1985) 439.

[421] K. Ventura, K. Komarek, J. Churacek (1985). Method and apparatus for the determination of functional groups by reaction chromatography using frontal technique. Pat Czech.; CS 211473 B 19840415; CAN: **102**, 72091; AN: **1985**, 72091.

[422] K. Ventura, K. Komarek, J. Choracek, J. Langhans, J. Safar, J. Salamoun (1985). *Use of analyzer CHN-1 in the analysis of fertilizers for the determination of nitrogen in various forms.* Chem. Prum, 35 (1985) 580-583; CAN: **104**, 87533; AN: **1986**, 87533.

[423] B. Waśkowski, S. Giziński (1985). *Insertion for combustion tube for elementary analysis of phosphoroorganic compounds.* Pat. PRL Nr. 126324.

[424] V.M. Zatonskaya, O.N. Koldobskaya, N.A. Gavrish (1985). *Use of analyzer CHN-3 for determination of carbon and nitrogen in different materials.* Zavod. Lab., 51 (1985) 11-12; CAN: **103**, 152868; AN: **1985**, 552868.

[425] A. Zigel, V.M Ryabnikova, O.G. Utkina, I.T. Korzhova (1985). *Use of CHN-2 analyzer for determination of the content of elements in organic substances and polymers.* Plast. Massy, **1985**, 43-45; CAN: **103**, 481100; AN: **1985**, 481100.

[426] B.H. Sheldrick (1986). *Test of the LECO CHN-600 determinator for soil CN analysis.* Can. J. Soil Sci., 66 (1986) 543-545; CAN: **105**, 58977; AN: **1986**, 589977.

[427] J.R. Sole, B. Colombo (1986). *Characterization of fuels. A study of the caloric value of solid and liquid fuels by the results of a CHN-OS elementary anlyzers.* Quim. Ind. (Madrid), 32 (1986) 119-121; CAN: **106**, 52880; CAN: **1987**, 52880.

[428] B. Waśkowski, R. Gondko, J. Kaczmarek (1986). *Simple integrating system coupled with gas chromatography and a pyrolysis attachment for elemental analysis.* Chem. Anal. (Warsaw), 31 (1986) 305-310.

[429] J. Kaczmarek, R.Gondko (1987). *Oxythermal mixtures in nitrogen determination in elementary analysis.* Chem. Anal. (Warsaw), 32 (1987) 131-136.

[430] E. Kristensen, F.O. Andersen (1987). *Determination of organic carbon in marine sediments; a comparison of two CHN-OS-analyzer methods.* J. Expl. Mar. Biol. Ecol., 109 (1987) 15-23; CAN: **107**, 161191; AN: **1987**, 561191.

[431] S. Lee, J.A. Fuhrman (1987). *Relations between biovolume and biomass of naturally derived marine bacterioplancton.* Appl. Environ. Microbiol., 53 (1987) 1298-1303; CAN: **107**, 45840; AN: **1987**, 45840.

[432] R.E. Mathews (1987). *Photooxidation of organic impurities in water using thin films of titanium dioxide.* J. Phys. Chem., 91 (1987) 3328-3333.

[433] S. Motomizu, K. Toei, T. Kuvaki, M. Oshima (1987). *Gas-diffusion unit with tubular microporous poly(tetrafluoroethylene) membrane for flow-injection determination of carbon dioxide.* Anal. Chem., 59 (1987) 2930-2932.

[434] G.A. Norton, N.S. Adams, R. Markuszewski, S.V. Brayton (1987). *Rapid dissolution technique for colorimetric determination of nitrogen in coals.* Fuel, 66 (1987) 996-1001; CAN: **107**, 99446; AN: **1987**, 499466.

[435] W. Stefańska, A. Postupolski, S. Rubel (1987). *On electrochemical deter-mination of carbon in waters and wastes. I. Potentiometric method after oxidation of organic matter by persulfate.* Chem. Anal., (Warsaw), 32 (1987) 919-927.

[436] M. Wasek, S. Sterliński (1987). Determination of nitrogen, phosphorus and potassium in food, fodder and fertilizers by fast neutron activation analysis. Chem. Anal. (Warsaw), 32 (1987) 137-150.

[437] L.V. Antisari, P. Sequi (1988). Comparison of total nitrogen determination by four procedures and sequential determination of exchangeable ammonium, organic nitrogen, and fixed ammonium in soil. Soil Sci. Soc. Am. J., 52 (1988) 1020-1023; CAN: **109**, 229400; AN: **1988**, 628400.

[438] T. Aoki, K. Ito, M. Munemori (1988). Determination of total nitrogen in water by chemiluminiscence: comparison of catalysts. Bunseki Kagaku, 37 (1988) 133-137; AA: 50 (1989) 2H 53.

[439] S.L. McGeehan, D.V. Naylor (1988). *Automated instrumental analysis of carbon and nitrogen in plant and soil samples.* Commun. Soil Sci. Plant Anal., 19 (1988) 493-505.

[440] J. Namieśnik (1988). *Total parameters for estimation of degree of environmental pollution. Methods and apparatus.* Chem. Anal. (Warsaw), 33 (1988) 835-860.

[441] I. Schneider (1988). *A rapid automatic elemental analysis.* Am. Lab., 20 (1988) 14; CAN: **110**, 177581; AN: **1989**, 177581.

[442] W.J. Swidall, D.T. Burns (1988). *Improvements to the CHN performance of a Carlo Erba 1106 elemental analyzer by blank evaluation, drift correction using a pair of dissimilar standards and modifications to the gas flow system.* Fresenius' Z. Anal. Chem., 331 (1988) 730-734.

[443] K. Ventura, K. Komarek, J. Churacek, J. Safar, R. Kreuzig (1988). *Estimation of nitrogen functional groups by reaction gas chromatography – frontal technique. Oximes, semicarbazones, nitroanilines and amino acids.* Chem. Pap., 42 (1988) 621-629.

[444] K. Ventura, K. Komarek, J. Churacek, H. Davidova, J. Langhans, J. Salamoun (1988). *Determination of nitrogen functional groups by reaction gas chromatography – frontal technique. Azoxy compounds, triazenes, pentaaza-1,4-diene derivatives.* Chem. Pap., 42 (1988) 773-780.

[445] S.W. Kubala, D.C. Tilotta, M.A. Busch, K.W. Busch (1989). *Determination of total inorganic carbon in aqueous samples with a flame infrared emission detectors.* Anal. Chem., 61 (1989) 1841-1846.

[446] R. Siegfried (1989). *Determination of proteins and total nitrogen using FP-228 in comparison with other methods.* Fresenius' Z. Anal. Chem., 335 (1989) 489-492.

[447] Z. Vecera, V. Rezl (1989). *Simultaneous determination of CHNS by reaction gas chromatography.* Chem. Listy, 83 (1989) 546-550.

[448] V. Rezl, A. Buresova (1989). *Simultaneous CHN determination by oxygen balance during combustion.* Anal. Sci., 6 (1990) 375-378; CAN: **113**, 108536; AN: **1990**, 508536.

[449] T.W. Walsch (1989). *Total dissolved nitrogen in seawater: a new high-temperature combustion method and a comparison with photo-oxidation.* Mar. Chem., 26 (1989) 295-311; CA: 111 (1989) 160369.

[450] A. Aminot, B. Kerouel (1990). *Improvement of a commercial continuous-flow method for the determination of dissolved organic carbon in fresh water and seawater.* Analusis, 18 (1990) 289-295.

[451] G.K.C. Low, R.W. Mathews (1990). *Flow-injection determination of organic organic contaminants in water using an ultra-violet-mediated titanium dioxide film reactor.* Anal. Chim. Acta, 231 (1990) 13-20.

[452] R.W. Mathews, M. Abdullah, G.K.C. Low (1990). *Photocatalytic oxidation for total organic carbon analysis.* Anal. Chim. Acta, 233 (1990) 171-179.

[453] A.N. Shkil, A.B. Krasnushkin, I.T. Gaveilow (1990). *Simultaneous deter-mination of dissolved organic forms of carbon and phosphorus in natural waters with photochemical oxidation of organic matter by low-pressure mercury lamps.* Zh. Anal. Khim., 45 (1990) 1615-1623.

[454] I. Steffen, J. Nuss, P. Schrammel (1990). *Determination of nitrogen and carbon in soil and plants.* GIT Fachz. Lab., 34 (1990) 1457-1459; CAN: **114**, 100317; AN: **1991**, 100317.

[455] S.I. Sverdlova, V.M. Ryabikova (1990). *Determination of carbon and hydrogen in fluoro-polymers using CHN-1 automatic analyzer.* Plast. Massy, **1990**, 70-72; CAN: **114**, 63146; AN: **1991**, 63146.

[456] A. Bermond, C.J. Ducauze (1991). *Optimization of microwave mineralization of meat products for Kjeldahl nitrogen determination.* Analusis, 19 (1991) 64-66.

[457] C.B. Craft, E.D. Seneca, S.W. Broome (1991). *Loss on ignition and Kjeldahl digestion for estimating of organic carbon and total nitrogen in estuarine soils: calibration with dry combustion.* Estuaries, 14 (1991) 175-179; CAN: **115**, 255026; AN: **1991**, 655026.

[458] A. Farina, R. Piergallini, A. Doldo, E.P. Salsano, F. Abbale (1991). *The deter-mination of CHN by an automated elemental analyzer.* Microchem. J., 43 (1991) 181-190.

[459] S.A. Huber, F.H. Frimmel (1991). *Flow injection analysis of organic and inorganic carbon in the low-ppb range.* Anal. Chem., 63 (1991) 2122-2130.

[460] G. Kahnt (1991). *Application test of analytical analyzers.* LaborPraxis, 15 (1991) 132-138; CAN: **115**, 153132; AN: **1991**, 453132.

[461] V.P. Miroshina, E.M. Dubina (1991). *Catalyst for the oxidative decomposition of polycyclic organic substances in analysis with the automated HP CHN analyzer.* Zh. Anal. Khim., 46 (1991) 493-499.

[462] J.C. Yeomans, J.M. Bremmer (1991). *Carbon and nitrogen analysis of soils by automated combustion techniques.* Commun. Soil Sci. Plant Anal., 22 (1991) 843-850.

[463] M. Baccanti, P. Pagni, J. Theobald (1992). *Flash combustion.* Lab. Pract., 4 (1992) 25; AA: 55 (1993) 10H 376.

[464] G. Meier, G. Schmidt (1992). *Experience in the simultaneous determination of total nitrogen and ^{15}N by coupling nitrogen analyzers with the NOI-6 analyzer.* Isotopenpraxis, 28 (1992) 85-96; CAN: **120**, 3845; AN: **1994**, 3845.

[465] D.T. Burns (1993). *Precursors and evolution of elemental organic tube combustion analysis over last two hundred years.* Anal. Proc., 30 (1993) 272-275.

[466] M.H. Feinbergh, J. Ireland-Ripert, R.M. Mourel (1993). *Optimization procedure of open vessel microwave digestion for Kjeldahl nitrogen determination in foods.* Anal. Chim. Acta, 272 (1993) 83-96.

[467] C. Girardin, A. Mariotti (1993). *Automated analysis system for ^{13}C natural abundance measurement in organic carbon.* Cah. ORSTOM, Ser. Pedol., 16 (1993) 371-380; CAN: **121**, 279652; AN: **1994**, 679652.

[468] R.R. Jimenez, J.K. Ladha (1993). *Automated elemental analyses: a rapid and reliable but expensive measurement of total carbon and total nitrogen in plant and soil samples.* Commun. Soil Sci. Plant Anal. 24 (1993) 1897-1924.

[469] H. Kroon (1993). *Determination of nitrogen in water: comparison of a continuos-flow method with online UV digestion with the original Kjeldahl method.* Anal. Chim. Acta, 276 (1993) 287-293.

[470] I. Matejovic (1993). *Determination of carbon, hydrogen and nitrogen in soils by automated analysis (dry combustion method).* Commun. Soil Sci. Plant. Anal., 24 (1993) 2213-2222.

[471] I.D. McKelvie, M. Mitri, B.T. Hart, I.C. Hamilton, A.D. Stewart (1994). *Analysis of total dissolved nitrogen in natural waters by online photooxidation and flow injection.* Anal. Chim. Acta, 293 (1994) 155-162.

[472] H.A. McKenzie (1994). *Kjeldahl determination of nitrogen – retrospect and prospect.* TrAC, Trends Anal. Chem., 13 (1994) 138-144; AA: 56 (1994) 8D 109.

[473] J.T. Riley, S.C. Burris, J.M. Stidam, A. Wu, D. Zhang (1994). *Utilization of elementar analysis in university laboratories.* Am. Lab., 26 (1994) 15-16; CAN: **122**, 203958; AN: **1995**, 235530.

[474] K. Robards, I.D. McKelvie, R.L. Benson, P.J. Worsfold, N.J. Blundell, H. Casey (1994). *Determination of carbon, phosphorus, nitrogen and silicon species in waters.* Anal. Chim. Acta, 287 (1994) 147-190.

[475] G. Demortier (1995). *Analysis of light elements with a nuclear probe.* Nucl. Instrum., Methods Phys. Res., Sect B, B 104 (1995) 244-254.

[476] T. Kupila-Rantala, M. Hyvonen-Dabek, J.T. Dabek, J. Raisanen (1995). *Assessment of the usefulness of the PIGE method to determine nitrogen in human blood serum.* J. Radioanal. Nucl. Chem., 196 (1995) 145-152; AA: 58 (1996) 2F 17.

[477] N.I. Larina, A.G. Buyanovskaya (1995). *Determination of nitrogen by Kjeldahl digestion and colorimetric titration.* Zh. Anal. Khim., 50 (1995) 1217-1219.

[478] S. Norland, K.M. Fagerbakke, M. Heldal (1995). *Light element analysis of individual bacteria by X-ray analysis.* Appl. Environ. Microbial., 61 (1995) 1357-1362; CAN: **122**, 234 625; AN: **1955**, 479613.

[479] J. Martin, Y. Takahashi, M. Datta (1995). *A dual-channel analyzer for the determination of nitrogen in water.* Am. Lab., 27 (1995) 49-53; AA: 57 (1995) 10H 86.

[480] I. Matejovic (1995). *Total nitrogen in plant material determined by means of dry combustion: a possible alternative to determination by Kjeldahl digestion.* Commun. Soil Sci. Plant. Anal., 26 (1995) 2217-2229.

[481] S. Motomizu, M. Sanada (1995). *Photo-induced reduction of nitrate to nitrite and its application to the sensitive determination of nitrate in natural waters.* Anal. Chim. Acta, 308 (1995) 406-412.

[482] M. Yamamuro, H. Kayanine (1995). *Rapid direct determination of organic carbon and nitrogen in carbonate bearing sediments with a Yanaco MT-5 CHN analyser.* Limnol. Oceanogr., 40 (1995) 1001-1005; CAN: **123**, 295916; AN: **1995**, 853458.

[483] H. Albrich, M. Niveller (1996). *Determination of total bound nitrogen by Dumas combustion and chemiluminiscence determination.* LaborPraxis, 20 (1996) 92-95; AA: 58 (1996) 11H 71.

[484] J. Golimowski, R. Golimowska (1996). *UV photo-oxidation as pretreatment step in inorganic analysis of environmental samples.* Anal. Chim. Acta, 325 (1996) 111-133.

[485] B. Fry, E.T. Peltzer, C.J. Hopkinson, A. Nolin, L. Redmond (1996). *Analysis of marine DOC using a dry combustion method.* Mar. Chem., 54 (1996) 191-201; AA: 59 (1997) 5H 99.

[486] Y. Furokawa, K. Yokoyama, K. Inoue, K. Ishibashi, H. Fukuyama (1996). *A compact wavelength-dispersive X-ray spectrometer for particle-induced X-ray emission analysis.* Nucl. Instrum. Methods Phys. Res., Sect. B, B 118 (1996) 372-376; AA: 59 (1997) 7C 21.

[487] D. Lee, V. Nguyen, S. Littlefield (1996). *Nitrogen determination in organic compounds. Comparison of Kjeldahl vs Dumas methods.* Commun. Soil Sci. Plant Anal., 27 (1996) 783-793; AA 58 (1996) 6H 152.

[488] E.T. Peltzer, B. Fry, P.H. Doering, J.H. McKenna, B. Norrman, U.L. Zweifel (1996). *A comparison of methods for the measurement of DOC in natural water.* Mar. Chem., 54 (1996) 65-96; AA: 59 (1997) 4H 137.

[489] H. Shi, J.T.B. Strove, L.T. Taylor, E.M. Fujinari (1996). *Feasibility of supercritical-fluid chromatography-chemiluminiscent nitrogen detection with open tabular columns.* J. Chromatogr. A, 734 (1996) 303-310.

[490] W. Stefańska, S. Rubel (1996). *Potentiometric and coulometric determination of total organic carbon in water samples.* Chem. Anal. (Warsaw), 41 (1996) 1015-1023.

[491] B.V. Stolyarov, L.A. Kratsova, O.M. Evstingneeva (1996). *Determination of total organic nitrogen in soils, plant materials and aqueous media by exhaustive hydrogenolysis. A modified procedure.* Zh. Anal. Khim., 51 (1996) 1097-1103.

[492] K. Vandepuite, L. Moens, R. Dams (1996). *Improved sealed-tube combustion of organic samples to carbon dioxide for stable carbon isotope analysis, radiocarbon dating and percent carbon determinations.* Anal. Lett., 29 (1996) 2761-2773; AA: 59 (1997) 3D 173.

[493] R.B. Willis, M.E. Montgomery, P.R. Allen (1996). *Improved Kjeldahl method for manual, colorimetric determination of total organic nitrogen using salicilate.* J. Agric. Food Chem., 44 (1996) 1804.

[494] E. Ballesteros, A. Rios, M. Valcarec (1997). *Integrated automatic determi-nation of nitrate, ammonium and organic carbon in soil samples.* Analyst, 122 (1997) 309-313.

[495] I. Bator, V. Schneeweiss, R. Winkler (1997). *Nitrogen protein determination in flour and grain.* GIT Labor.-Fachz., 41 (1997) 612-615; AA: 60 (1998) 2H 248.

[496] M.E. Birch, R.A. Cary (1997). *Elemental and organic carbon by thermal-optical method.* Aerosol Sci. Technol., 25 (1996) 221-225; AA: 59 (1997) 01H 136.

[497] A. Cerda, M.T. Oms, R. R. Fortena, V. Cerda (1997). *Total nitrogen determination by flow injection using online microwave-assisted digestion.* Anal. Chem. Acta, 351 (1997) 273-279.

[498] B.V. Ioffe, I. Zenkevich (1997). *Practical application and chemometrical evaluation of the algorithm of organic compound molecular formula determination according to data from elemental analysis without additional information.* Vest. Sankt.-Petersburg Univ., Ser. 4, Fizyka, Khimiya, **1997**, 74-79; CAN: **128**, 289519; AA: **1998**, 179046.

[499] K. Lueuhder (1997). *The role of selenium in mixed catalysts for Kjeldahl digestion of pyridine derivatives.* Chem. Anal. (Warsaw), 42 (1997) 603-604.

[500] I. Mateiovic (1997). *Determination of carbon and nitrogen in samples of various soils by the dry combustion.* Commun. Soil Sci. Plant Anal., 28 (1997) 1499-1511; AA: 60 (1998) 6H 172.

[501] S. Motomizu, M. Oshima, L. Ma (1997). *On-site analysis for phosphorus and nitrogen in environmental samples by flow-injection spectrophotometric method.* Anal. Sci., 13 (1997) 401-404; AA: 60 (1998) 7H 68.

[502] M.J. Navas, A.M. Jimenez, G. Galan (1997). *Air analysis: determination of nitrogen compounds by chemiluminiscence.* Atmos. Environ., 31 (1997) 3605-3608; AA: 60 (1998) 7H 37.

[503] F. Papillon, P. Walter (1997). *Analytical use of the multiple gamma-rays from the* $^{12}C(d,p)^{13}C$ *nuclear reaction.* Nucl. Instrum. Meth.ods Phys. Res. Sect. B, B 132 (1997) 468-480; AA: 60 (1998) 6D 109.

[504] O. Schmidt, W.R. Fischer (1997). *Calibration of the electrochemical oxidation of organic carbon compounds in solution.* GIT Labor-Fachz., 41 (1997) 268-269; AA: 59 (1997) 11H 75.

[505] H. Salah, B. Touchrift (1997). *Multielemental analysis of zeolites.* Nucl. Instrum. Methods Phys. Res. Sect. B, B 129 (1997) 261-265.

[506] J.H. Sharp (1997). *Marine dissolved carbon: are the older values correct?* Mar. Chem., 56 (1997) 265-277; AA: 59 (1997) 10H 100.

[507] A.H. Simonne, E.H. Simonne, R.R. Eitenmiller, H.A. Mills, C.P. Cresman (1997). *Could the Dumas method replace the digestion for nitrogen and crude protein determination in foods.* J. Sci. Food Agric., 73 (1997) 39-45; AA: 59 (1997) 7H 229.

[508] A. Skoog, D. Thomas, R. Lara, K.U. Richter (1997). *Methodological investigations on DOC. Determinations by the high-temperature catalytic oxidation (HTCO) method.* Mar. Chem., 56 (1997) 39-44; AA: 59 (1997) 9H 89.

[509] X.L. Su, L.H. Nie, S.Z. Yau (1997). *Determination of ammonia in Kjeldahl digests by gas-diffusion flow-injection analysis with a bulk acoustic wave impedance sensor.* Talanta, 44 (1997) 421-428.

[510] J. You, M.A. Dempster, R.K. Marus (1997). *Analysis of organic compounds by particle-hollow cathode atomic-emission spectroscopy.* Anal. Chem., 69 (1997) 3419-3426.

[511] M. Woerner, H.P. Sieper (1997). *Determination of nitrogen in food by Dumas combustion. Instrument for nitrogen-protein determination.* Labor Praxis, 21 (1997) 90-92; AA: 60 (1998) 6H 239.

[512] X.A. Alvarez-Salgado, A.J. Miller (1998). *Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation condition for precise shipboard measurements.* Mar. Chem., 62 (1998) 325-333; AA: 61 (1999) 4H 112.

[513] J. Anon (1998). *Total organic carbon in a six pack.* Labor Praxis, 22 (1998) 14; AA: 60 (1988) 1H 185.

[514] Z. Chemat, D.J. Hadj-Boussato, F. Chemat (1998). *Application of atmospheric-pressure microwave-digestion to total Kjeldahl nitrogen determination in pharmaceutical, agricultural and food products.* Analusis, 26 (1998) 205-209.

[515] M. LeClerc, J. Van der Plicht, H.A.J. Meijer (1998). *A supercritical oxidation system for the determination of carbon isotope ratios in marine sediments.* Anal. Chim. Acta, 370 (1998) 19-27.

[516] A. Doyle, J.P. Schimel (1998). *Dichromate digestion and simultaneous colorimetry of microbial carbon and nitrogen.* Soil Sci. Soc. Amer. J., 621 (1998) 937-941; AA: 61 (1999) 1H 158.

[517] S. Duffin (1998). *Analysis of lead compounds – key to drug development.* Lab. Update, **1998**, 10-11; AA: 61 (1999) 4D 90.

[518] G. Heltai, K. Debreczeni, A. Balint, E. Notas, Z.A. Tarr, T. Jozsa (1998). *Analytical and methodological development of ^{15}N tracer technique for soil nitrogen transformation studies.* Soil Sci. Plant Anal., 29 (1998) 1875-1890; AA: 60 (1998) 12H 182.

[519] K. Ishlam, R.R. Weil (1998). *A rapid microwave-digestion method for colorimetric measurement of soil organic carbon.* Commun. Soil Sci. Plant Anal., 29 (1998) 2269-2289; AA: 61 (1999) 2H 120.

[520] J. Kanda, K. Sada, Z. Koike, K. Yokouchi (1998). *Application of an automated C-N analyzers for elemental and isotopic analysis of samples retained on glass-fiber filters.* Int. J. Environ. Anal. Chem., 72 (1998) 169-171; AA: 62 (2000) 6H 226.

[521] H. Kempert, Q. Sprinkhuisen, A. Van Strien (1998). *Innovative and automatic analysis of total bound nitrogen.* Labor Praxis, 22, (1998) 84-87; AA: 61 (1999) 4H 107.

[522] I.G. Parker, S.D. Kelly, M. Sharman, M.J. Dennis, D. Howie (1998). *Investigation into the use of carbon isotope ratios (carbon-13/carbon-12) of scotch whisky congeners to establish authenticity using GC-combustion-isotope ratio Mass Spectrometry.* Food. Chem., 63 (1998) 423-428; AA: 61 (1999) 4H 305.

[523] N. Takahata, Y. Nishio, N. Yoshida, Y. Sano (1998). *Precise isotopic measure-ments of nitrogen at the sub-nanomole level.* Anal. Sci., 14 (1998) 485-491; AA: 60 (1998) 11D 68.

[524] N.F.Y. Tan, W.Y. Yao (1998). *An accurate, simple and novel analytical method for the determination of total organic carbon in sediment.* Int. J. Environ. Anal. Chem., 72 (1998) 137-150; AA: 62 (2000) 6H 225.

[525] D.L. Wang, D.W. Anderson (1998). *Direct measurement of organic carbon content in soil by the LECO CR-12 carbon analyzer.* Commun. Soil Sci. Plant Anal., 29 (1998) 15-21; AA 60 (1998) 9H 146.

[526] P.G. Wiles, I.K. Gray, R.C. Kissling (1998). *Routine analysis of protein by Kjeldahl and Dumas method.* J. AOAC Int., 81 (1998) 620-632; AA 60 (1998) 11H 358.

[527] V.P. Yakovchenko, L.J. Sikora (1998). *Modified dichromate method for determining of low concentration of extractable organic carbon in soil.* Commun. Soil Sci. Plant Anal., 29 (1998) 421-433; AA: 60 (1998) 9H 144.

[528] M. Colina, P.H. Gardner (1999). *Simultaneous determination of total nitrogen, phosphorus and sulfur by microwave digestion and ion chromatography.* J. Chromatogr. A, 847 (1999) 285-290.

[529] E. Daffner, S. de Galan, L. Goyens (1999). *Microwave digestion of organic substances. A useful tool for dissolved nitrogen measure means.* Water Res., 33 (1999) 548-554; AA: 61 (1999) 7H 26.

[530] S. Krishan, W.C. Sturtridge (1999). *Nitrogen determination in human body, by neutron activation analysis.* J. Radioanal. Nucl. Chem., 239 (1999) 71-77; AA: 61 (1999) 7F 40.

[531] L.S. Leong, P.A. Turner (1999). *Comparison of methods of determination of organic carbon in marine sediments.* Marine Pollution Bull., 38 (1999) 875-879; CAN: **132**, 355800; AN: **1999**, 777803.

[532] J.L. Lima, M.C. Montenegro, A.P. Pinto (1999). *Determination of total nitrogen in food by flow-injection analysis with potentiometric differential detection.* Fresenius' J. Anal. Chem., 364 (1999) 353-357.

[533] H. Liu, Y. Yang (1999). *Determination of nitrogen content in crude oil and heavy distillates by CHN-O-elementary analysis.* Shiou Huagong, 28 (1999) 781-783; CAN: **132**, 4580; AN: **1999**, 776477.

[534] H. Matusiewicz, B. Golik, A. Suszka (1999). *Determination of residue carbon content in biological and environmental samples by microwave-induced-plasma atomic emission spectroscopy.* Chem. Anal. (Warsow), 44 (1999) 559-566.

[535] P. Raimbault, F. Diaz, W. Pouvesele, B. Boudjellal (1999). *Simultaneous determination of particulate organic carbon, nitrogen and phosphorus collected on filters, using a semi-automatic wet-oxidation method.* Marine Ecology, 180 (1999) 289-295: CAN: **132**, 68945; AN: **2000**, 16389.

[536] C.H. Shreier, W.J. Walker, J. Burns, R. Wikenfield (1999). *Total organic carbon as a screening method for petroleum hydrocarbon.* Chemosphere, 39 (1999) 503-510; AA: 62 (2000) 2H 88.

[537] L. Stryer (1999). *Biochemistry*, 4-th ed. WNPWN S.A., Warsaw, 1999.

[538] S.Z. Yao, X.L. Su (1999). *Gas diffusion flow-injection analysis with bulk acoustic wave detection and the applications for determining nitrogen, carbon and sulfite species.* J. AOAC, 82 (1999) 1479-1487; AA: 62 (2000) 5D 51.

[539] R.A. Werner, B.A. Bruch, W.A. Brand (1999). *ConFlo III – an interface for high precision $\delta^{13}C$ and $\delta^{15}N$ analysis with an extended dynamic range.* Rapid Commun. Mass Spectrom., 13 (1999) 1237-1241; CAN: **131**, 124708; AN: **1999**, 446855.

[540] A. Ammann, T.B. Reuttimann, F. Buergi (2000). *Simultaneous determination of total organic carbon and total bound nitrogen in surface water by optimizes high-temperature catalytic combustion.* Water Res., 34 (2000) 3573-3579; AA: 63 (2001) 3H 130.

[541] K. Hecker (2000). *Differentiation between total carbon and total organic carbon in solids by difference and direct methods.* GIT Labor-Fachz., 44 (2000) 1156-1157; AA: 63 (2001) 4H 173.

[542] U. Kathe (2000). *Thermocatalytic oxidation in TOC analysis of super pure water.* J. Int. Lab. News, 30 (2000) 20-25.

[543] G.L. Kerven, N. Menzies, M.D. Geuer (2000). *Soil carbon determination by high-temperature combustion – a comparison with dichromate oxidation procedures and the influence of charcoal and carbonate carbon on the measured values.* Commun. Soil Sci. Plant Anal., 31 (2000) 1935-1939; AA: 63 (2001) 3H 179.

[544] B. Kovacs, J. Prokisch, Z. Gyori, A.B. Kovacs, A.J. Palencsar (2000). *Studies on soil sample preparation for inductively-coupled plasma atomic emission spectrometry analysis.* Commun. Soil Sci. Plant Anal., 31 (2000) 1949-1963; AA: 63 (2001) 3H 180.

[545] J. Parus, J. Kierzek, B. Małożowska-Bucko (2000). *Determination of the carbon content in coal and ash by wavelength-dispersive X-ray fluorescence method.* X-Ray Spectrom., 29 (2000) 192-195.

[546] R.L. Paul, R.M. Lindstrom (2000). *Prompt gamma-ray activation analysis: fundamentals and analysis.* J. Radioanal. Nucl. Chem., 243 (2000) 181-189; AA: 62 (2000) 7D 25.

[547] J.B. Reeves, G.W. McCarry, V.S. Reeves (2000). *Mid-infra-red diffuse refluctance spectroscopy for the quantitative analysis of agricultural soils.* J. Agric. Food Chem., 49 (2000) 768-772.

[548] G. Spyres, M. Nimno, P.J. Worsfold, E.P. Achterberg (2000). *Determination of dissolved organic carbon in seawater using high-temperature catalytic oxidation.* Trends Anal. Chem., 19 (2000) 498-506; AA: 62 (2000) 12H 147.

[549] T. Stratesteffen, K. Pospisil (2000). *Expecience of performance qualification in total organic carbon analysis of water for pharmaceutical use.* GIT Labor-Fachz., 44 (2000) 1134-1135; AA: 63 (2001) 4G 12.

[550] R. Winkler (2000). *Analysis of solid samples in suspension for TOC and TBN.* GIT Labor-Fachz., 44 (2000) 123-126; AA: 62 (2000) 8H 272.

[551] R. Winkler (2000). *Analysis of protein nitrogen in fluids by the Dumas method.* GIT Labor-Fachz., 44 (2000) 278-279; AA: 62 (2000) 8H 272.

[552] E.N. Carrilho, A.R. Noglueira, J.A. Nobrega, G.B. de Souza, G.H. Cruz (2001). *An attempt to correlate fat and protein content of biological samples with residual carbon after microwave assisted digestion.* Fresenius' J. Anal. Chem., 371 (2001) 336-340.

[553] R. Cerrera (2001). *Total organic carbon (TOC) – the advantages and closed loop technology.* Inst. Envir. Technol., 10 (2001) 18-19; AA: 63 (2001) 7D 74.

[554] M. Confalowieri, F. Fornaster, A. Ursino, F. Boccardi, B. Pintus, M. Odoardi (2001). *The potential of near-infra-red reflectance spectroscopy as a tool for characterization of agricultural soils.* J. Near Infrared Spectrosc., 9 (2001) 123-131; AA: 64 (2002) 5H 164.

[555] Y. Gou (2001). *Determination of total nitrogen in water samples by spectrophotometry using phenol after alkaline peroxydate digestion.* Bunseki Kagaki, 50 (2001) 481-486; AA: 64 (2002) 3H 76.

[556] S.T. Gouivera, F.W. Silva, L.M. Coista, A.R. Nogueuira, J.A. Nobrega (2001). *Determination of residual carbon by inductively-coupled plasma optical emission spectrometry with axial and radial view configuration.* Anal. Chim. Acta, 445 (2001) 269-275.

[557] R.A.W. Johnstone, M.E. Rose (2001). *Mass spectrometry.* WN PWN, Warsaw, 2001.

[558] A. Jungnickel, S. Foerster (2001). *Determination of total organic carbon in solid materials.* GIT Labor-Fachz., 45 (2001) 360-362; AA: 63 (2001) 11D 50.

[559] C.G. Kowalenko (2001). *Assessment of LECO CNS-2000 analyzer for simultaneous measuring total carbon, total nitrogen and total sulfur in soil.* Commun. Soil Sci. Plant Anal., 32 (2001) 2065-2078; AA: 64 (2002) 3H 174.

[560] H. Matusewicz (2001). *Critical evaluation of effectiveness of nitric acid oxidizing systems: pressurized microwave-assisted digestion procedure.* Chem. Anal. (Warsaw), 46 (2001) 897-905.

[561] J.M. O'Meara, B.W. Blackburn, D.L. Chichester, D.P. Gierga, J.C. Yanch (2001). *The feasibility of accelerator-based in vivo neutron-activation analysis of nitrogen.* Appl. Radiat. Isot., 55 (2001) 767-774; AA: 64 (2002) 8F 13.

[562] C. Mouse (2001). *Two in one: flexible total organic carbon analysis.* GIT Labor-Fachz., 46 (2002) 164; AA: 64 (2002) 12D 27.

[563] M. Palocz-Andresen (2001). *Quick and simple total nitrogen determination.* GIT Labor-Fachz., 25 (2001) 44-47; AA: 64 (2002) 5H 109.

[564] J.N. Paniz, E.M. Flores, V.L. Dressler, A.F. Martins (2001). *Flow-injection turbidimetric determination of total organic carbon with a gas-liquid transfer microreactor.* Anal. Chim. Acta, 445 (2001) 139-144.

[565] J.P. Reeves, G.W. McCarthy (2001). *Quantitative analysis of agriculture soils using near infrared reflectance spectroscopy and a fibre optic probe.* J. Near IR Spectrosc., 9 (2001) 25-34; AA: 64 (2002) 2H 141.

[566] B. Sebatic, J. Balenovic (2001). *Rapid ecologically acceptable method for wheat protein content determination. Comparison of methods.* Dtsch. Lebensm.-Rundsch., 97 (2001) 221-225; AA: 64 (2002) 1H 148.

[567] R.J. Shypailo, K.J. Ellis (2001). *Estimation of bacground interference in prompt-gamma neutron using MCNP.* J. Radioanal. Nucl. Chem., 249 (2001) 407-412; AA: 64 (2002) 6F 11.

[568] M. Tran, Q. Sun, B.W. Smith, J.D. Winefordner (2001). *Determination of carbon : hydrogen : nitrogen : oxygen ratios in solid organic compounds by laser-induced plasma spectroscopy.* J. Anal. At. Spectrom., 16 (2001) 628-632; AA: 64 (2002) 2D 86.

[569] U. Traeger (2001). *Total organic carbon monitoring in high-purity water systems. What is behind it?* GIT Labor-Fachz., 45 (2001) 714-716; AA: 64 (2002) 3H 164.

[570] E.T. Urbansky (2001). *Total organic carbon analyzers as tools for measuring carbonaceous matter in natural water.* J. Environ. Monitor., 3 (2001) 102-112; AA: 63 (2001) 9H 140.

[571] R. Willemsen, A. Benelux (2001). *CHNOS analysis is now relatively simple.* J. Neth. Chemisch-2-Weekblad, 97 (2001) 16-17; CAN: **135**, 70258; AN: **2001**, 222141.

[572] A.F. Wright, J.S. Bailey (2001). *Organic carbon, total carbon and total nitrogen determination in soils of variable calcium carbonate contents using a LECO CN-2000 dry combustion analyzer.* Commun. Soil Sci. Plant Anal., 32 (2001) 3243-3258; AA: 64 (2002) 08H 98.

[573] T. Yasuhara, K. Nokihara (2001). *High-throughput analysis of total organic nitrogen that replaces the classic Kjeldahl method.* J. Agric. Food Chem., 49 (2001) 4581-4583.

[574] M. Defernez, H.S. Taap, E.K. Kemsley, R.H. Wilson (2002). *Opthotermal (OT) spectroscopy: a photoacoustic technique.* Am. Lab., 34 (2002) 34-38; AA: 64 (2003) 05 H 1.

[575] B. Demirata, R. Apak, H. Afsar, I. Tor (2002). *Spectrometric determinations of organic nitrogen by a modified Lassaigne method and its application to meat products and baby food.* J. AOAC Int., 85 (2002) 971-977; AA: 64 (2003) 05 H 424.

[576] J.M. Lynch, D.M. Barbano, D.R. Flening (2002). *Determination of total nitrogen of hard, semihard and processed chese by Kjeldahl method. Collaborative study.* J. AOAC Int., 85 (2002) 444-456; AA: 64 (2003) 02 H457.

[577] A. Marco, R. Rubio, R. Compano, I. Cassalo (2002). *Comparison of the Kjeldahl method and combustion method for total nitrogen determination in animal feed.* Talanta, 57 (2002) 1019-1026.

[578] E. Norlin, K. Irgum, K.E.A. Ohlson (2002). *Determination of* N^{15}/N^{14} *ratio of ammonium and ammonia in aqueous solutions by headspace-gas chromatography-combustion-isotope ratio by mass spectrometry.* Analyst, 127 (2002) 735-740.

[579] B. Wallace, M. Purcell (2002). *The benefit of monitoring nitrogen by high temperature combustion.* J. Int. Lab. News, 32 (2002) 24-27.

[580] B. Waśkowski, Z.H. Kudzin, W. Ciesielski, P. Kowalski (2003). *Determination of nitrogen in organic compounds and biological samples by gas chromatography after prior degradation into molecular nitrogen with use of solid oxidants.* Chem. Anal. (Warsaw) 48 (2003) 223-232.

[581] Technical bulletin of CHN-1 analyzer (LPP-Praha, CSSR).

[582] Carlo Erba, Divisione Apparachi Scientifici, Milano, Italy; Model CHN – M 1104, technical bulletin.

[583] www.thermofinnigan.com.

[584] Perkin Elmer, Corp. Norwalk, Conn. USA; Model 240 – technical bulletin.

[585] www.instruments.-perkinelmer.com.

[586] Heraus G.m.b.h., 6450 Hanau, Germany.

[587] www.instruments.herausgmbh.com.

[588] www.elementar.de

[589] www.eurovector.it.

[590] Hewlett-Packard, F&M Scientific Division, Avondale, PA 1931, USA; Model F&M 185; technical bulletin

[591] www.instruments-hewlettpackard.com.

[592] Technicon Corp., Torrytown, NY 10591, USA

[593] Compagnie Technicon France – B.P. No 10 Domont 95330.

[594] www.eail.com.

[595] www.costech.net/

[596] www.leco.com.

[597] www.leco.com/organic/chn-analyzers/TruSpec-CHN.htm

[598] www.leco.com/customersupport/apps/appnotes.htm

[599] www.danispa.it/eng/prodotti_labnoratorio_gascromatografi.asp

[600] Antek Instruments Inc., Houston, Texas 77090; Digital Nitrogen Analyzers, Models 703 and 720; technical bulletin.

[601] www.antek.se/laboratory.htm

[602] www.antekhou.com.

[603] www.mandel.ca/products/supplier.html

[604] www.shimadzu.com/

[605] www.ssi.shimadzu.com/products

[606] www.sel.shimadzu.com/products

[607] www.eu.shimadzu.de/products/analytica/toc

[608] Evirotech-Dohrman; Total Nitrogen Analyser; models DN-10, DN-100; technical bulletins.

[609] Evirotech-Dohrman; Microcoulometric Titration System; model MCTS-10; technical bulletin.

[610] www.ench.ucalgary.ca/environ/instrument.html

[611] Mitsubishi Chemical Industries, Ltd.; Total Nitrogen Analyzer; model TN-05; technical bulletin.

[612] www.instruments.mitsubishi.com.

[613] B. Waśkowski (2004). *Analysis of nitrogen. Nitrogen analyser.* Ph. D. Dissertation book. University of Łódź.

CA = Chemical Abstracts, AA = Analytical Abstracts, CAN and AN – abstract system applied in the Sci Finder Scholar base.