TRENDS IN ELEMENTAL ANALYSIS OF ORGANIC COMPOUNDS

Edmund Kozłowski

Technical University of Gdańsk, 80-952 Gdańsk, Poland

Abstract - Beginning from the breakthrough period during 1960-1970 four main trends can be distinguished in elemental analysis of organic compounds: 1. development of automated and computerized analytical procedures, 2. introduction, particularly in large laboratories, of computerized on-line systems of parallelly coupled automated analytical procedures, 3. intensive development of methods for simultaneous determinations including attempts to perform complete elemental analysis in one sample and 4. increase of interest in systems for direct combination of elemental analysis with separation techniques including multielemental analysis of components of complex mixtures of organic compounds using a microwave plasma emission spectrometer as an element-selective detector. The present state-of-art, perspectives and possibilities of these trends are discussed and illustrated on the basis of recent developments dealing with obtaining information about the elemental spectrum comprising ten of the fundamental nonmetallic constituents in organic compounds.

1. INTRODUCTION

Modern organic elemental analysis can be defined as an area of Analytical Chemistry dealing with optimal strategies of obtaining relevant information about elemental spectrum of organic materials, both pure compounds and/or technical and natural products and organic environmental pollutants. Hence, elemental analysis of organic compounds or components of their mixtures constitutes an essential area of broadly defined organic elemental analysis providing fundamental data about new compounds or data for identification of known compounds in the form of direct and unambiguous information about their elemental composition (Ref. 1). Modern methods permit to obtain the information about the entire elemental spectrum and particularly the ten fundamental nonmetallic constituents in organic compounds (Ref. 2). However, calculating the necessary information quantity of one- or more-dimensional analysis, according to Griepink and Dijkstra (Ref. 3), time and expenses required should also be taken into account. This is associated with an appropriate choice of methods and their degree of automation and/or computerization according to the tasks performed, especially in large analytical laboratories. Among many categories of the proposed definitions of Analytical Chemistry (Ref. 4) the problem of broadly defined strategy both in practice and in choice of new directions should be pointed out. Today, elemental analysis is no more the only source of information about the elemental spectrum of organic compounds (Ref. 5), thus, it must remain competitive with respect to other methods and in further development it should take into account new trends in organic chemistry and technology and in the analysis of organic environmental pollutants. More and more frequently model syntheses are carried out on a micro scale and new compounds isolated from natural products or synthesized, e.g., organometallic compounds, often constitute a multicomponent mixture. Hence, reliable methods are required for wide concentration range - from macro to trace constituents and the scale of determination should be adequate to the degree of nonhomogeneity of a sample with the possibility of analysis of components of complex mixtures of organic compounds.

2. DEVELOPMENT OF ORGANIC ELEMENTAL ANALYSIS

Modern trends in organic elemental analysis can be best illustrated against
a background of almost two hundred years of history of its development by
many generations of analytical chemists. The authors of all, even most
significant papers, cannot be mentioned here or selected literature cited in
the paper discussed closer due to the abundance of information.

2.1. Basic development stages

The rate of development of organic elemental analysis is exponential with
respect to shortening duration periods of successive fundamental stages
(Fig.) 1 : from macroanalysis initiated by Gay-Lussac and Thénard who first
employed a vertical combustion tube (Ref. 1, 5), through classical microana-
lysis originated by Pregl to ultramicroanalysis the development of which has
been an international endeavor (Ref. 6-12). The latter constitutes a crowning
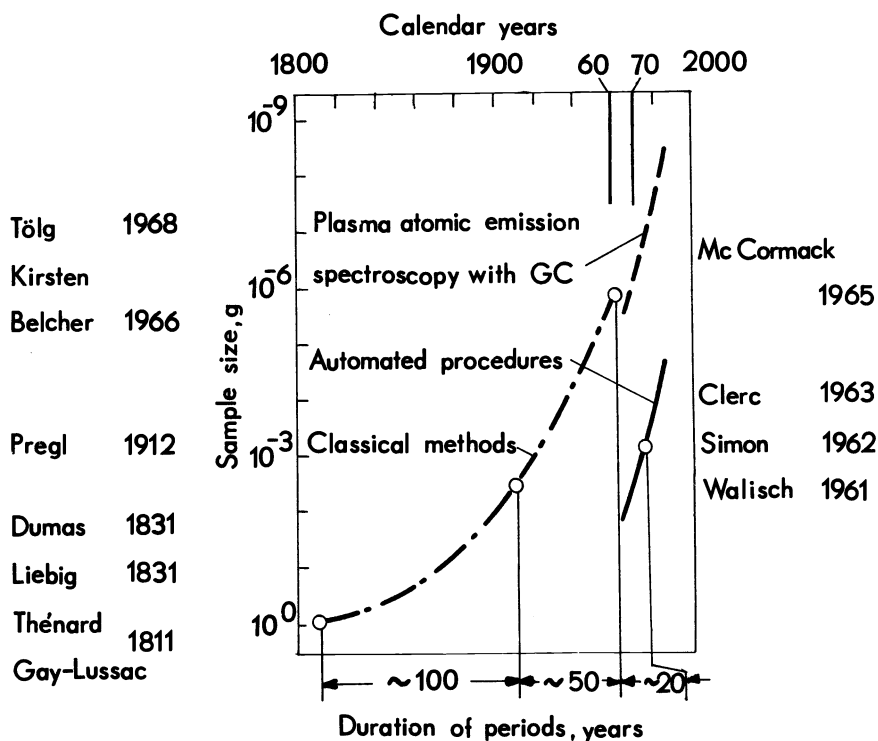achievement of classical microanalysis.

Fig. 1. Graphical illustration of exponential rate of
development of organic elemental analysis. Breakthrough
between 1960 and 1970 should be noted. Basic development
stages are indicated. Further explanation in the text .

Breakthrough occurred in the sixties and seventies. Then, a new stage of
automated analytical procedures has begun (Ref. 13-15) which in the case of
automated determination of carbon and hydrogen has been completed during ca.
20 years. In 1962 Simon (16) at the ILMAC Conference (Internationale
Fachmesse und Fachtagungen für Laboratoriumstechnik, Messtechnik und
Automatic in der Chemie) in Basel specified the requirements for the
automated determination of these elements and already in 1979 Ma' and Rittner
(17) estimated that...the automated apparatus for the determination of carbon
and hydrogen have passed their developmental stage... (see the point on solid
curve in Fig. 1). Also in the sixties McCormack et al. (18) initiated the
application of microwave plasma atomic emission spectroscopy for detection of
gas chromatographic effluents which constitutes a new approach to multiele-
mental analysis of multicomponent mixtures of organic compounds (see
paragraph 6.2).

Introduction of automated apparatus and widespread use of simple and

inexpensive flask combustion technique as well as the development of spectroscopic methods of structural investigations resulted in temporary decrease in interest in elemental analysis. This is reflected by the number of papers which in the first half of the seventies remained at a similar level (Fig. 2). However, during 1978-1982 the number of papers doubles, and particularly those dealing with the simultaneous determinations and trace analysis. This is especially the effect of increase in the application of methods of elemental analysis for the determination of nonmetallic elements as well as metalloids and metals in a variety of organic materials (Ref. 19-25).
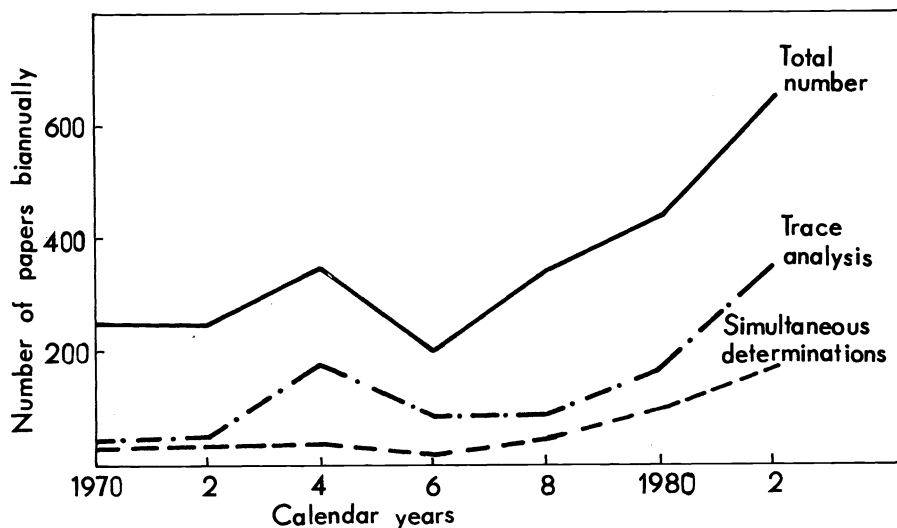

Fig. 2. Number of papers on organic elemental analysis published biannually. Total number of papers (————), including: number of papers concerning trace determinations of single elements (— · —) and number of papers dealing with simultaneous determinations (— — —), excluding simultaneous determination of carbon and hydrogen. Data extracted from the biannual fundamental reviews of Ma et al. (Ref. 19-25).

2.2. The main trends in elemental analysis of organic compounds
Classical approach to elemental analysis is under growing influence of the "development pressure" which is illustrated by arrows in Fig. 3. This classical approach is characterized by the simultaneous determination of carbon and hydrogen with separate methods for the determination of the remaining main constituents of organic compounds and by the many steps of the process of analysis. A general trend tends to decrease the number of analytical procedures required to obtain the information about the elemental spectrum of a substance as well as to reduce the number of steps of the analysis and to eliminate manual operations associated with it. The resulting four main trends in elemental analysis of organic compounds (illustrated by arrows) are listed in the caption under Fig. 3.

3. AUTOMATED AND COMPUTERIZED ANALYTICAL PROCEDURES

The initiation of trends aiming at automation of the analysis and at simultaneous determinations are methods of determination of carbon, hydrogen and nitrogen in one sample which have been developed during the last twenty years. Modern analyzers based on these methods are highly automated and computerized including data processing (Ref. 26-29). Presently, these are reliable methods of general applicability (Ref. 25), suitable - as recently demonstrated by Culmo (30) - even for the analysis of such refractory substances as graphitic carbon and silicon carbide by adding a thermal accelerator to the sample. Gelman et al. (31) have shown the possibility of using the analyzer based on reaction frontal gas chromatography for the analysis of various heteroorganic and organometallic compounds. Utilization of a thermal conductivity detector as a uniform method of final determination
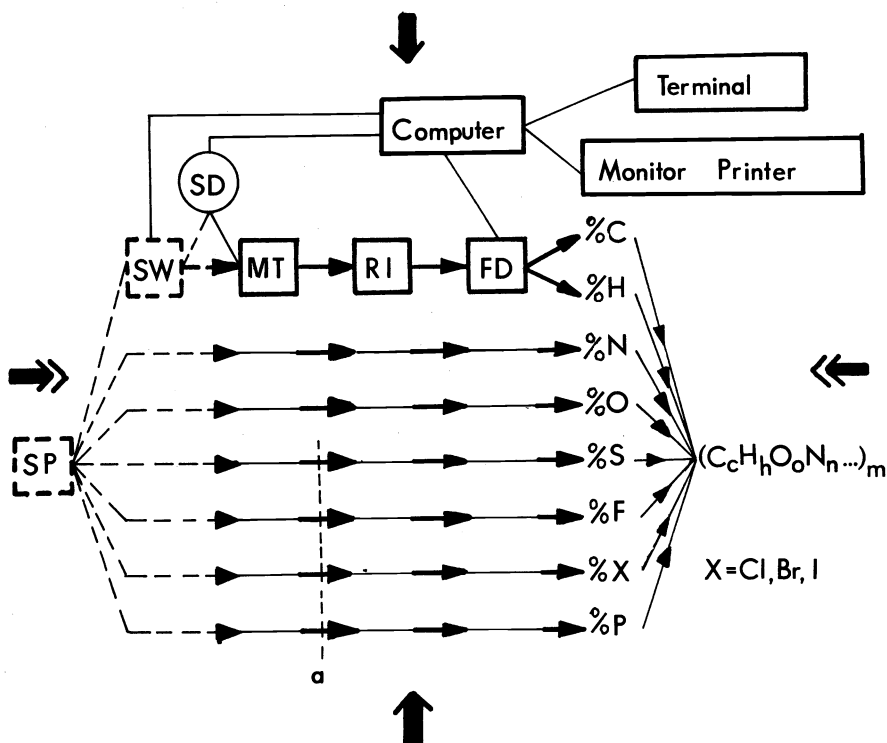
Fig. 3. Illustration of the development pressure on the classical approach to elemental analysis of organic compounds. SP - sample preparation, SW - sample weighing, SD - sample dispenser, MT - mineralization technique, RI - removal of interferences, FD - final determination. Automatic run (———), manual operations (— — —), a - interruption of automatic run by using flask combustion.
Arrows illustrate the directions of the four main trends:
1. (→ or ◄)- automated and computerized analytical procedures for determination of single or several elements,
2. (⇒)- computerized on-line systems of parallelly coupled automated analytical procedures,
3. (↕)- methods for simultaneous multielement determination including attempts to perform complete elemental analysis from one sample,
4. (⇒◄)- direct combinations of elemental analysis with separation techniques including continuous multielemental analysis of complex mixtures.

permitted to considerably extend the scale of determinations down in comparison with classical microanalysis, limiting at the same time the possibility of analysis of larger samples. Characteristic are recent attempts to extend the scale of determinations upwards which would enable direct analysis of inhomogeneous substances without the need of tedious additional homogenization of samples. The limits of applicability of a thermal conductivity detector (Ref. 32, 33) can be extended by determining independently and successively one after another the three components in the combustion products (Ref. 34) and by using a calibration curve determined by a least-squares method in the form of forth degree polynomial (Ref. 35). This formed the basis for extension of applicability of a carbon, hydrogen and nitrogen analyzer (Ref. 34) and, recently, also a nitrogen analyzer (Ref. 36) up to centigram samples. According to Merz (35), accurate results were obtained for all three elements. The analysis of still larger samples would require the increase in volume of the combustion train, but then - as pointed out by Tölg et al. (37) - the ratio of surface to sample becomes unfavorable. This

problem can be solved by controlling the combustion rate (Ref. 37, 38). A truly automatic method, based upon self-regulation of the rate of combustion process by specific behavior of a substance during heating and associated with it pressure changes in a combustion tube was proposed by Bobrański (39, 40) already in 1928.

Besides possibilities of utilization of carbon, hydrogen and nitrogen analyzers also for the determination of oxygen and/or sulfur (Ref. 28, 41), the progress in development of automated analytical procedures for the determination of halogens (Ref. 42, 43) and sulfur (Ref. 44) is slower (see also para. 4). The use of the flask combustion technique and its modifications enabling the final determination to be carried out without transfer of solution from the flask (Ref. 45-47) still predominates in the determination of heteroelements. This mineralization technique permits the automation of an analytical procedure only at the stage of final determination, although the method of its automation has also been described (Ref. 48). Final determinations are usually performed by titrimetric methods. Besides continuous titrations in the ultramicro range proposed by Griepink, Römer and van Oort (49), completely new possibilities are presently being opened before titrimetric methods. Utilization of titriprocessors (Ref. 50, 51) and automatic version of weight titrations creates a chance of attaining the precision higher by at least one order of magnitude (Ref. 52). This should lead to significant improvement in precision of the results of elemental analysis, since previous achievements in this area are incommensurable with the progress in automation and computerization of analytical procedures. Further collaborative testing (Ref. 53) based on new reference substances (Ref. 54) needed particularly for the estimation of accuracy of non-absolute methods is advised for full evaluation of new methods.

4. COMPUTERIZED ON-LINE SYSTEMS OF AUTOMATED ANALYTICAL PROCEDURES

The use of computers, not only in elemental analysis, becomes more and more common with the increase in availability of software and cheapening of hardware - especially in miniaturized form of so-called personal computers (Ref. 55). Introduction of computers, useful particularly in large laboratories (Ref. 56-61), reflects the trend aiming at the determination of all main constituents of organic compounds on the basis of a computerized on-line system of parallelly coupled automated analytical procedures. Such a system for the determination of carbon, hydrogen and nitrogen as well as of oxygen was introduced at the beginning of seventies by Maciak et al. (62) in Lilly Research Laboratories. During the following period the system was successively extended on the basis of the developed for this purpose (Ref. 63-65) unified analytical procedures for automated determinations of further elements (Fig. 4). The final determinations of sulfur and fluorine are based on colorostatic titrations, using a fiberglass optics colorimeter for the endpoint detection (Ref. 63, 64). Halogens are determined by argentometric titration to the preset endpoint potential measured with a combination silver microelectrode (Ref. 65). Instrumentation for the developed automated analytical procedures is inexpensive and can be based on the commercially available equipment appropriately adapted for the purpose (Fig. 5).

An essential step in the automated course of analysis is quantitative transfer of the combustion products from the outlet of the combustion tube into the titration vessel as well as their simultaneous conversion respectively into one form for the final determination. A modified wash technique was used for this purpose (Fig. 6). Aqueous solutions of hydrogen peroxide, sulfur dioxide and pure water were employed as wash solutions in the determination of sulfur, halogens and fluorine, respectively.

Fig. 7 illustrates the expanded (Ref. 62-66) computerized on-line system of all parallelly coupled automated analytical procedures in the Microanalytical Laboratory of the Lilly Research Laboratories. The analyzers are interfaced to the departmental real-time, time-sharing computer along with electronic microbalances. The developed analyzers are interfaced to the computer via pulse counters. The accumulated electronic pulses from the burettes are then transmitted to the computer and identified as to the unit number of the sample. Data from the balance and analyzer are calculated and reported to the operator on the CR terminal (Fig. 8). The format of the report was published (Ref. 62). A particular report of the analytical results is also stored on the magnetic disk for further processing. The central processing unit, operating in a time-sharing mode also services (on-line) the high resolution mass and automatic nuclear magnetic resonance spectrometers. The results of other
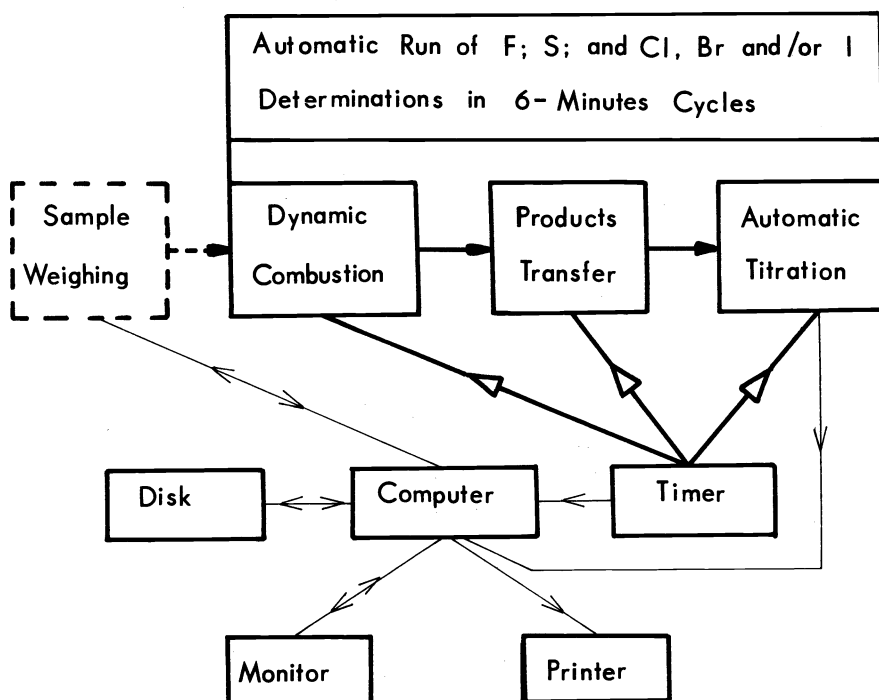
Fig. 4. Block diagram of computerized unified analytical proce-
dures for automatic determination of fluorine, sulfur and
halogens. Steps of analysis under cam switch timer control
(—▷—), manual operations (— — —), automatic run (———). The
preprogrammed 6 - min cycle comprises the entire analysis time
(5 minutes) as well as the automatic preparation of the titra-
tion assembly for the next determination - last minute.
(Ref. 66)

analyses can be transmitted to the computer off-line, recorded and used for
later processing. The analytical results obtained over a period of several
weeks as a daily instrument-control analysis are summarized in Table 1. Good
accuracy and precision of these data confirm at the same time the reliability
of the developed automated analytical procedures over a prolonged period of
time.

For further development of the system it is anticipated to provide it with
the automated method (Ref. 68) for identification of chlorine, bromine and
iodine determined argentometrically (Ref. 69). We suppose that it may also be
possible to develop an appropriate analytical procedure for the automated de-
termination of phosphorus. Hence, the computerized system would include the
spectrum of all ten nonmetallic elements (Fig. 3) being major constituents of
organic compounds. Similar computerized systems comprising determinations of
several elements were introduced during last years in a number of large
microanalytical laboratories (Ref. 58-61).

5. METHODS FOR SIMULTANEOUS MULTIELEMENT DETERMINATIONS

This is a trend aiming at the reduction of a number of analytical procedures
required to obtain the information about the elemental spectrum of the
analyzed compound. At the same time, this permits to utilize expensive
instrumentation to a greater extent. The number of papers dealing with this
subject is rapidly increasing (Fig. 2) and it is impossible even to cite all
the most important contributions. Gelman (70) listed gravimetric methods for
simultaneous determination of several elements distinguishing X-ray fluore-
scence as a non-destructive method of analysis of organometallic compounds.
The investigations of titrimetric methods for simultaneous determination of
several elements in the absorption solution after flask combustion are con-
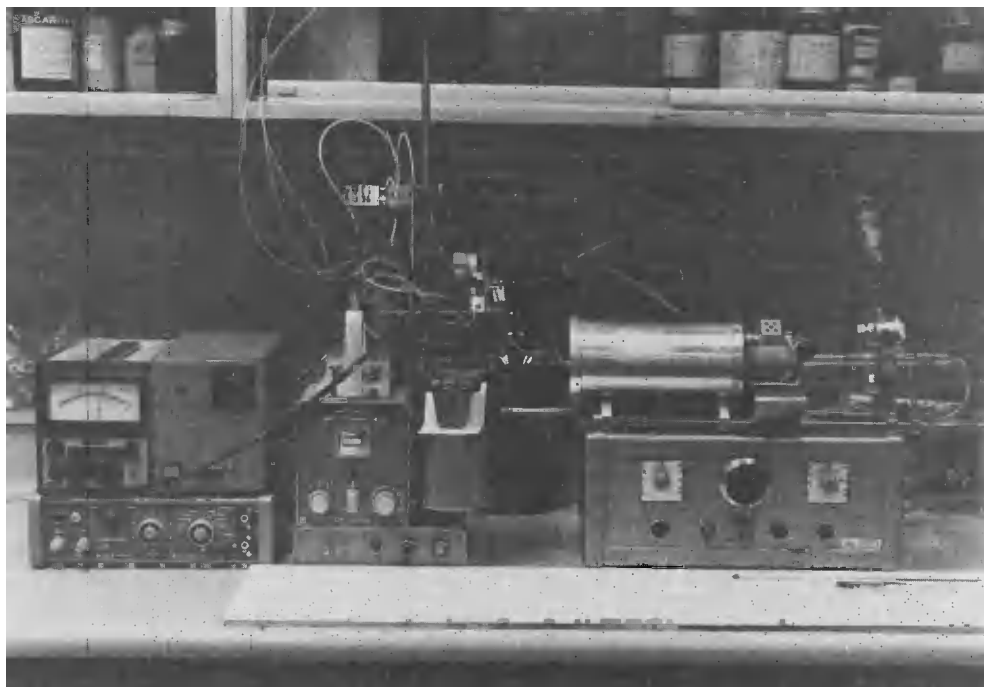
Fig. 5. Photograph of the apparatus for automated determination
of fluorine. From right to left: combustion train, automatic
titration assembly, cam switch timer, fiberglass colorimeter
and (below) potentiostat.

tinued (Ref. 71-73). New possibilities for automated multielemental final de-
terminations by a wet method are provided by the employment of modern ion
exchange chromatography with conductometric detection (Ref. 74, 75). Using
high performance ion exchange columns a number of ions can be separated in
several minutes (Ref. 76). The automated dry method for simultaneous determi-
nation of carbon, hydrogen, nitrogen and sulfur (Ref. 28, 77-80) is already
employed by Kirsten et al. (81) in routine practice for the analysis of
unweighed samples using a chosen element content, e.g. carbon, as an internal
standard.

5.1. Chain of methods of overlapping simultaneous determinations
Sample weighing is not only a manual step in automated course of analysis but
also a source of human errors and a time- and labour-consuming operation in
the case of analysis of liquid, viscous, gaseous, hygroscopic or unstable
substances. This difficult for automation step of analysis can be eliminated
in the case of complete elemental analysis in one sample. However. this
cannot be achieved for the majority of organic compounds. For this reason,
Häberli (82) proposed a combined method of calculations employing in addition
to the data obtained from simultaneous determination of carbon, hydrogen and
nitrogen in an unweighed sample, also the percentage contents of the
remaining elements determined from weighed samples. At the IV Polish
Conference on Analytical Chemistry in 1974 we proposed (83) the calculation
of the results of analysis with complete elimination of sample weighing. This
can be achieved by using such a group of methods of simultaneous determina-
tion by which at least one of elements determined by any of the used methods
is again determined by another method and so on (Fig. 9).

Using developed by us methods for simultaneous determination of carbon,
hydrogen, nitrogen, sulfur and halogens in various combinations (Ref. 85-87),
this approach was experimentally tested (Table 2) for the case of complete
elemental analysis of six compounds. For the analyzed compounds containing in
a molecule from 1 to 21 atoms among six elements in various combinations
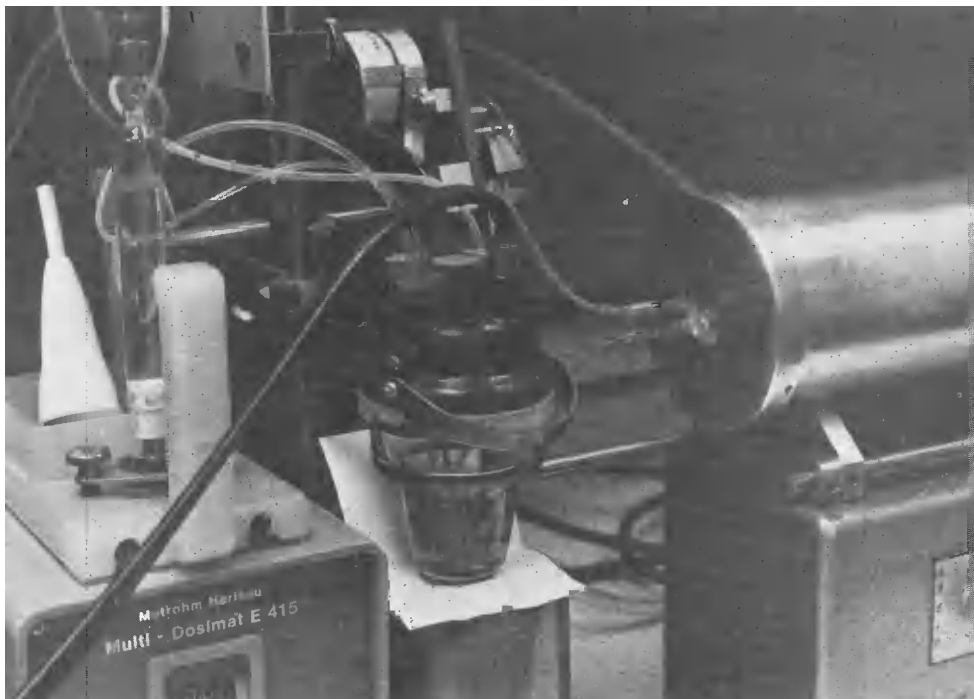satisfactory results were obtained. The high value of the pooled standard

Fig. 6. Photograph of the modified combustion tube with one-piece wash arrangement for quantitative transfer of combustion products into the titration vessel. The wash solution is pumped in a direction opposite to the oxygen flow.

deviation for the stoichiometric coefficient of hydrogen confirms the need for increasing precision of determination of this element (Ref. 88).

For the extension of this approach on all major constituents of organic compounds the methods enabling simultaneous determination of oxygen or phosphorus together with other elements are particularly needed. Rezl et al. (89-91) developed for this purpose the methods permitting simultaneous determination of carbon, hydrogen, nitrogen, oxygen and sulfur in various combinations (see also para. 6.1).

5.2. Attempts to perform complete elemental analysis in one sample
The desire to carry out complete elemental analysis in the same sample by means of one analytical procedure becomes more and more real. In a number of papers recently published Hara et al. (92-101) proposed a new method called pyrolytic sulfurization gas chromatography (Fig. 10).

The sample mixed with sulfur and sodium sulfide in a helium atmosphere is pyrolyzed in a sealed quartz ampule. The ampule is then crushed and the gaseous products and the aqueous extract are analyzed according to the scheme in Fig. 10. The possibility of simultaneous determination of oxygen in addition to the three main constituents of organic compounds is interesting in this method. Although the elements are determined in the form of multicomponent gaseous mixture, the results obtained had the absolute error in the range of ca. $\pm$ 0.2% abs. for various types of the analyzed organic compounds. Characteristic feature of this approach to multielemental analysis is parallel utilization of two chromatographic techniques for the separation of combustion products and two universal detectors for the final determinations.

The possibility of attaining complete elemental analysis from a single sample is so attractive that Sels (102) resumed the pioneer work of Walisch and Jaenicke (103-105) and van Leuven (106, 107) using for the detection of combustion products a mass spectrometer in which ions of different mass are separately determined (Fig. 11). The assembly is controlled by a microcompu-
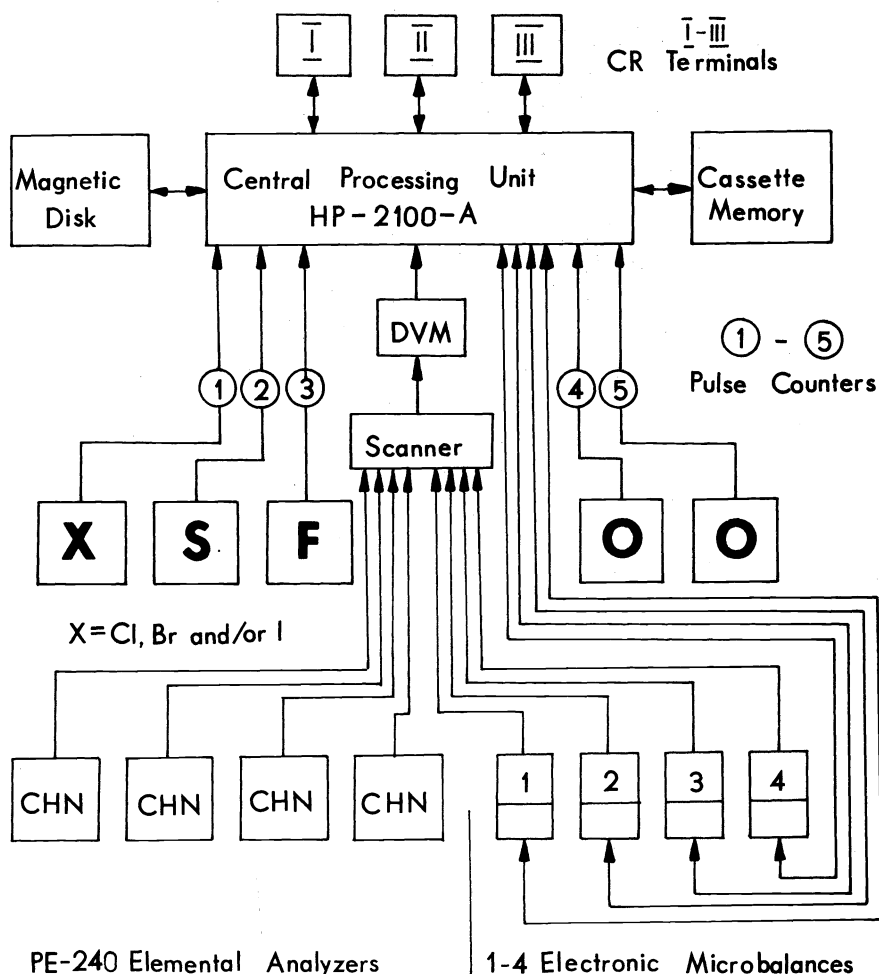
Fig. 7. Schematic block diagram of the computerized on-line
system of parallelly coupled analytical procedures for automa-
ted determination of a spectrum of nine of the main major
constituents in organic compounds (Ref. 66). The determination
of oxygen is based on the automated method described by Merz
(67).

ter in a relatively simple program for repeatability assessment. In model
investigations high repeatability was attained for three compounds which
permits the author of this method to expect the development of a rapid and
inexpensive procedure for routine analyses of various organic materials.

6. COMBINATION OF ELEMENTAL ANALYSIS WITH SEPARATION TECHNIQUES

This trend expresses the attempts to reduce the number of steps in elemental
analysis of mixtures of organic compounds by elimination of operations
associated with sample preparation and weighing. The problem of more and more
frequent need for the analysis of multicomponent mixtures can be solved by
using modern chromatographic techniques for the separation of components and
performing their elemental analysis without prior isolation of the separated
compounds. In this case the sample size is in the microgram range, that is at
the same level as in trace analysis. The determination of elemental composi-
tion of individual components in organic micropollutants in water is an
extreme example of trace elemental analysis of complex mixtures of organic
compounds (see para. 6.2).

Fig. 8. Photograph of a stand for weighing of samples and communication with a computer. The analyzer (upper left) is in the direct reach of an operator.
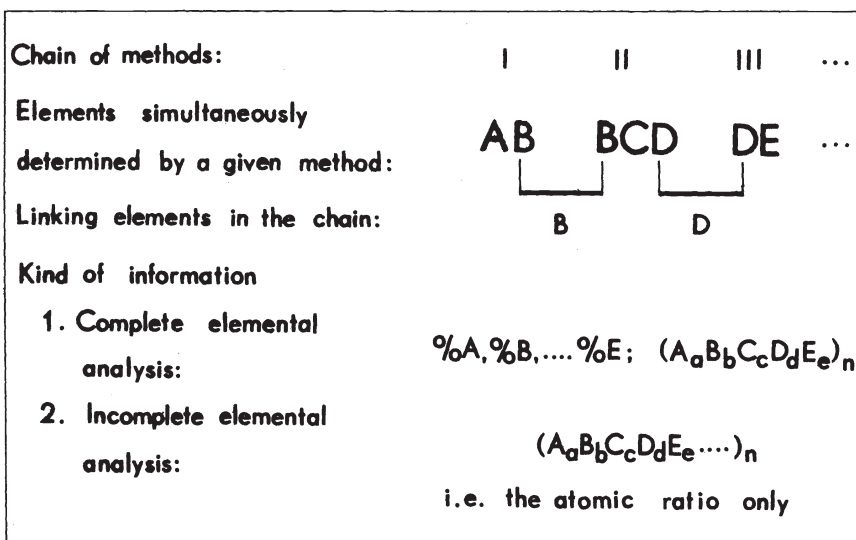

Fig. 9. General scheme of so-called chain of methods of overlapping simultaneous determinations for elemental analysis without weighing of samples (Ref. 83, 84).

TABLE 1. Statistical evaluation of analytical results

Element	S	F	Cl	Br	I
Formula	$C_6H_{12}N_2O_4S_2$	$C_7H_5O_2F$ $C_9H_6O_2F_6$	$C_7H_5O_2Cl$	$C_7H_5O_2Br$	$C_7H_5O_2I$
Theoretical, %	26.69	13.56 43.82	22.64	39.75	51.17
Sample size, mg	1.8 – 4.9	1.5 – 9.2 1.5 – 2.9	3.2 – 4.7	3.3 – 6.1	4.3 – 7.0
Number of results	16	7 7	10	8	9
Mean error, abs.%	0.01	0.10 -0.04	- 0.01	0.00	-0.02
Standard deviation, abs. %	0.13	0.13 0.17	0.05	0.14	0.18

6.1. Elemental analysis of gas chromatographic effluents

Combinations of gas chromatography with spectroscopic techniques, e.g., high resolution mass- or nuclear magnetic resonance spectroscopy are expensive, need skilled operators and do not provide direct information about elemental composition. Inexpensive solution is a combination of gas chromatography with elemental analysis. This problem has been dealt with for twenty years. At the beginning of seventies Liebman et al. (108, 109) developed a commercially available analyzer for this purpose. Recently, Rezl (110) published an extensive review discussing various possibilities of solving this problem with special consideration of elemental analysis without weighing. Basing on the developed by Rezl et al. (89-91) analytical procedures which form a chain of methods of overlapping simultaneous determinations (see paragraph 5.1), a hypothetical system can be conceived (Fig. 12) which permits the determination of four of the main constituents in organic compounds.

6.2. Combination of chromatography with microwave plasma emission spectroscopy

One of the most effective approaches to simultaneous multielemental analysis of multicomponent mixtures of organic compounds seems to be the direct coupling of a chromatograph with a microwave plasma emission spectrometer as an universal element-selective detector, with the range of linear response often exceeding over three orders of magnitude and relative freedom from matrix effects (Ref. 111). The applicabilities of microwave induced helium (Ref. 112-115) and argon (Ref. 18, 116, 117) plasmas for determination of elemental composition of organic compounds were investigated. The extremely high temperature from 5000 to 10000 K provides an efficient means of thermally complete destruction of organic compounds and subsequent excitation of the resulting atomic species also in the case of refractory elements. Main constituents in organic compounds can be determined on the basis of measurement of emission of radiation in the ultraviolet and visible (Ref. 113, 118) regions. There also exists a possibility of determination of the four fundamental constituents of organic compounds: carbon, hydrogen, oxygen and nitrogen by emission in the near infrared and red spectral regions (Ref. 119). Windsor and Denton (116) determined the empirical formulas and elemental composition of halogenated hydrocarbons in gas chromatographic effluents obtaining the results within the error limits of ca. + 0.3% abs. Other authors also determined nonmetallic (Ref. 112, 113, 115, 116) and metallic (Ref. 114, 117) elements in the effluents from gas- (Ref. 112, 113-116) and

TABLE 2. Summarized data on statistical evaluation of analyti-
cal results obtained by a chain of methods of overlapping
simultaneous determinations without weighing of samples
(Ref. 84).

Element			Element content, abs. %		Stoichiometric coefficient	
			Mean	Standard	Mean	Standard
	m	n	error	deviation	error	deviation
C	6 – 21	18	-0.06	0.17	+0.01	0.11
H	4 – 21	21	+0.05	0.12	+0.13	0.16
N	1 – 6	12	+0.09	0.14	+0.02	0.02
S	1	6	-0.04	0.13	0*	0*
X	1	15	-0.07	0.06	0*	0*

m - number of atoms in the formula of the compounds analyzed
n - number of determinations
0* - S or X (Cl or Br) were chosen as the reference elements
     for which the stoichiometric coefficient was set equal to
     unity

$$C^* \rightarrow CO_2 + COS + CS_2$$

$$H \rightarrow H_2S$$

$$O^* \rightarrow CO_2 + COS$$

$$N \rightarrow N_2$$

Pyrolytic
Sulfurization
(Sample + S + Na_2S)

$$Cl \rightarrow NaCl$$

$$Br \rightarrow NaBr$$

$$I \rightarrow NaI$$

GC — TCD → C, H, O, N
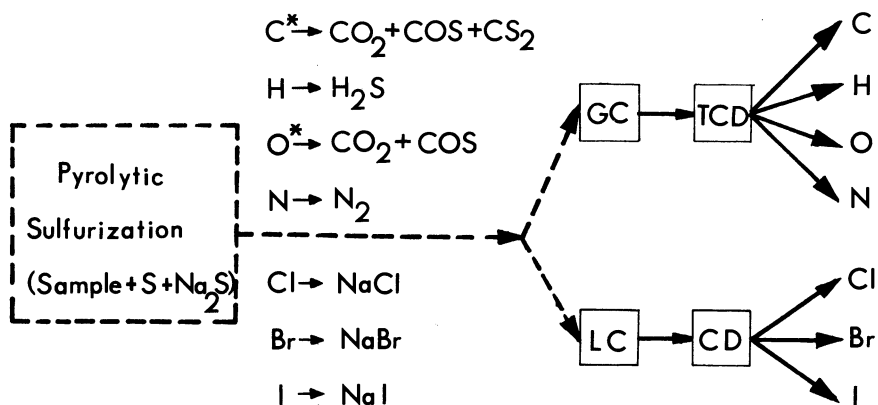
LC — CD → Cl, Br, I

Fig. 10. Simplified diagram of the principle of the pyrolytic
sulfurization method for simultaneous determination of seven
elements in organic compounds. GC - gas chromatograph, TCD -
thermal conductivity detector, LC - ion exchange liquid
chromatograph, CD - conductivity detector. Manual operations
(— — —).
C^x, O^x - if the atomic ratio of carbon to oxygen in the analy-
zed sample is lower than one additional products, water and
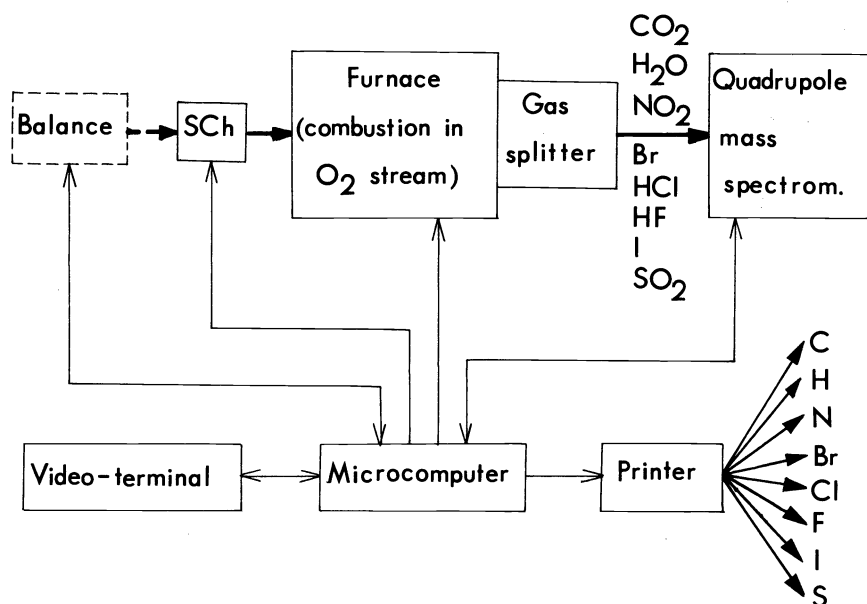sulfur dioxide, are formed (Ref. 92-101).

Fig. 11. Simplified block diagram of apparatus and method for simultaneous determination of eight elements in organic compounds, SCh - sample changer. Manual operations (— — —) (Ref. 102).
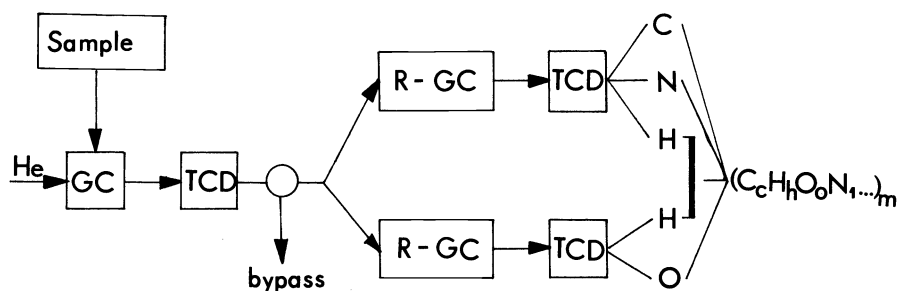
Fig. 12. Scheme of a hypothetical system for elemental analysis of gas chromatographic (GC) effluents without weighing of samples using two methods of overlapping simultaneous determinations based on reaction frontal gas chromatography (R-GC) with thermal conductivity detectors (TCD).

high-performance liquid chromatographic (Ref. 117) columns. The effluents were introduced into a high frequency plasma discharge tube or in an argon inductively coupled plasma (ICP) torch. Simultaneous determinations of several elements were accomplished by the use of a polychromator or a direct-reading spectrometer (Ref. 111). The number of papers on this new approach is rapidly increasing and as an example the work of Yu et al. (113) on simultaneous determination of an elemental spectrum including all the ten main nonmetallic constituents in multi-component mixtures of volatile organic compounds can be presented (Fig. 13). Satisfactory empirical formulas were obtained for test substances of various elemental composition containing up to 16 carbon atoms in a molecule.

Stieglitz et al. (115) described the application of combination of a gas chromatograph with a microwave plasma detector for the identification and quantitative determination of four volatile chlorinated hydrocarbons consti-
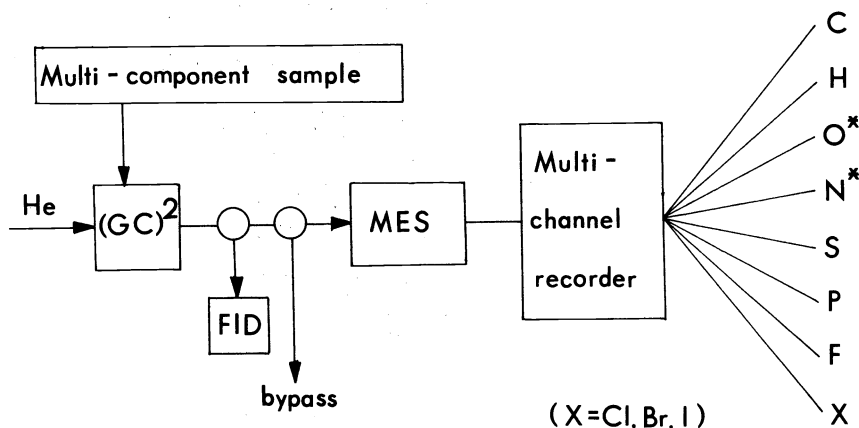
```
                  ┌──────────────────────────┐                                    C
                  │  Multi - component  sample │                                   /
                  └──────────────────────────┘                                  / H
                               │                                              / /
                               ↓                                           / / O*
            ┌─────┐    ┌───┐           ┌─────┐    ┌────────┐           / / /
     He  ──→│(GC)²│──→ │   │──→│   │──→│ MES │──→ │ Multi - │─────────── N*
            └─────┘    └───┘   └───┘   └─────┘    │ channel │           \ \ \
                         │       │                │         │             \ \ S
                         ↓       ↓                │ recorder│               \ \
                      ┌─────┐                     └────────┘                 \ P
                      │ FID │                                                  \
                      └─────┘                                                   \ F
                                                                                \
                         bypass              ( X = Cl, Br, I )                    X
```

Fig. 13. Simplified block diagram of on-line combination of a
high resolution glass capillary gas chromatograph (GC)² with
a microwave plasma emission spectrometer (MES). FID - flame
ionization detector for peak identification in the gas
chromatographic effluents.
O* , N* - low selectivity obtained (Ref. 113).

tuting organic micropollutants in river water. The identification of these
compounds was facilitated by the found carbon/chlorine ratio.

With increasing interest in multielemental analysis of organic compounds in
one sample a reasonably priced universal elemental analyzer based on
microwave plasma emission spectroscopy may offer in the future a general so-
lution to this problem.

7. SUMMARY AND CONCLUSIONS

The four main trends in elemental analysis of organic compounds presented in
this work have already been initiated during the breakthrough period in
1960-1970. The progress attained in the area of these trends concerning the
determination of elemental spectrum including ten main nonmetallic consti-
tuents in organic compounds is distinctly differentiated..

Automated apparatus for the determination of carbon and hydrogen have passed
their developmental stage. Automated and computerized analytical procedures
for simultaneous determination of carbon, hydrogen and nitrogen as well as
nitrogen alone have reached high degree of development and a general range of
applicability recently also for centigram samples. For the analysis of still
larger samples the introduction of automatic control of combustion rate is
necessary. Large progress has also been attained in automated analytical
procedures for the determination of oxygen and sulfur. Automated methods for
the determination of the remaining heteroelements are not being developed so
rapidly. Semi-automated procedures based on the flask combustion technique as
an inexpensive and flexible method, enabling also the determination of
metalloids and metals, are still widely employed for this purpose.

Further introduction of computerized on-line systems should be expected
together with the expansion of those already existing, as reliable automated
analytical procedures for the determination of the remaining elements are
being developed, since it is virtually impossible to conceive modern elemen-
tal analysis without a computer and data processing, especially in large
analytical laboratories.

The interest in methods of simultaneous determinations in one sample is
rapidly increasing. A practically useful automated analytical procedure
for the simultaneous determination of carbon, hydrogen, nitrogen and sulfur
has already been developed. Further development of the methods permitting
simultaneous determination of oxygen in addition to other main constituents
in organic compounds are particularly needed. At the present developmental

stage other methods of simultaneous determination of many elements are still not competitive in comparison with the methods of their separate determination with respect to the reliability, labour and/or costs.

The methods for simultaneous multielement determinations are more and more needed for the analysis of multicomponent mixtures. Unquestionable usefulness of the result in the form of total content of one or more elements in the analysis of organic materials becomes insufficient in many cases of the analysis of a mixture of organic compounds. Basic solution of this problem is to determine the complete elemental spectrum of individual components of the mixture, which can be achieved by direct combination of elemental analysis with modern techniques of separation of organic compounds using a microwave plasma emission spectrometer as an element-selective detector. Atomic emission spectroscopy opens before multielemental analysis of organic compounds quite new possibilities. However, the introduction of this technique to routine elemental analysis of organic compounds requires still more investigations. Additionally, the problem of cost of such a solution in comparison with the existing methods remains open.

Despite the enthusiasm for physical methods of analysis it should also be kept in mind - as pointed out by Kienitz (120) - that chemical methods are in their variety almost inexhaustible. The use of ion exchange chromatography provides new possibilities of simultaneous determinations by wet methods. The possibilities of titrimetric methods of final determinations are also far from being exhausted. Utilization of titroprocessors and a new technique of weight titrations permits to develop not only new automated analytical procedures but also creates a chance of significant improvement of precision of the results which would constitute fundamental progress in elemental analysis of organic compounds. In the light of various possibilities which result from the trends discussed here and the increase in degree of complexity of tasks performed, a strategic outlook on further development of elemental analysis as well as rational organization and a scope of laboratory equipment, particularly in large centers of investigations of organic compounds, becomes more and more needed.

REFERENCES

1. B. Bobrański, _Quantitative Analysis of Organic Compounds (in Polish)_, PWN, Warszawa (1979).
2. F. Ehrenberger and S. Gorbach, _Methoden der organischen Elementar- und Spurenanalyse_, Verlag Chemie, Weinheim (1973).
3. B. Griepink and G. Dijkstra, _Z. Anal. Chem._ 257, 269-272 (1971).
4. G. Kateman and A. Dijkstra, _Z. Anal. Chem._ 297, 249-253 (1979).
5. B. Bobrański, _Wiadomości Chem._ 36, 425-442 (1982).
6. R. Belcher, _Submicro Methods of Organic Analysis_, Elsevier, Amsterdam (1966).
7. W.J. Kirsten and K. Hozumi, _Microchem. J._ 6, 591-599 (1962).
8. W.J. Kirsten, _Microchem. J._ 7, 34-40 (1963).
9. W.J. Kirsten, B. Danielson and E. Ohren, _Microchem. J._ 12, 177-185 (1967).
10. W.J. Kirsten, _Microchem. J._ 12, 307-320 (1967).
11. G. Tölg, _Chemische Elementaranalyse mit kleinsten Proben_, Verlag Chemie, Weinheim (1968).
12. W. Merz and W. Pfab, _Mikrochim. Acta_ 1969, 905-920.
13. W. Walisch, _Chem. Ber._ 94, 2314-2327 (1961).
14. W. Simon, P.F. Sommer and C.H. Lyssy, _Microchem. J._ 6, 239-258 (1962).
15. J.T. Clerc and W. Simon, _Microchem. J._ 7, 422-436 (1963).
16. W. Simon, _Chimia_ 16, 312-321 (1962).
17. T.S. Ma and R.C. Rittner, _Modern Organic Elemental Analysis_, Marcel Dekker, New York (1979), p. 49.
18. A.J. McCormack, S.S.S. Tong and W.D. Cooke, _Anal. Chem._ 37, 1470-1476 (1965).

19. T.S. Ma and M. Gutterson, Anal. Chem. 42, 105R-114R (1970).
20. T.S. Ma and M. Gutterson, Anal. Chem. 44, 445R-457R (1972).
21. T.S. Ma and M. Gutterson, Anal. Chem. 46, 437R-451R (1974).
22. T.S. Ma and M. Gutterson, Anal. Chem. 48, 101R-106R (1976).
23. T.S. Ma and M. Gutterson, Anal. Chem. 50, 86R-92R (1978).
24. T.S. Ma and M. Gutterson, Anal. Chem. 52, 42R-50R (1980).
25. T.S. Ma, C.Y. Wang and M. Gutterson, Anal. Chem. 54, 87R-96R (1982).
26. D.E. Harrington and W.R. Bramstedt, Microchem. J. 21, 60-69 (1976).
27. W.R. Bramstedt and D.E. Harrington, Microchem. J. 24, 158-167 (1979).
28. B. Colombo and G. Giazzi, Anal. Chem. 52, 2112-2116 (1979).
29. D.T. Burns, H.B. MacKnight, R.K. Quigg and W.J. Swindel, Analyst 105, 544-550 (1980).
30. R.F. Culmo, Pittsburgh Conference Paper No. 205 (1981) - private commun. March 1983.
31. L.M. Kiparenko, N.E. Gelman, N.D. Maslenikova and V.I. Smirnova, Zh. Analit. Khim. 35, 328-334 (1980).
32. V. Rezl, Mikrochim. Acta 1982II, 107-114.
33. G. Bartelmus and W. Heussler, Z. Anal. Chem. 312, 221-226 (1982).
34. H. Eipper and F. Schölz, 8th International Microchem. Symp., Graz (1980), Abstracts, p. 77.
35. W. Merz, private commun. April 1983.
36. B. Colombo and G. Giazzi, Int. Lab., Sept. (1982), 76-84.
37. G. Knapp, S.E. Raptis, G. Kaizer, G. Tölg, P. Schramel and B. Schreiber, Z. Anal. Chem. 308, 97-103 (1981).
38. I.J. Oita, R.F. Babcock, Anal. Chem. 52, 1007-1008 (1980).
39. B. Bobrański and E. Sucharda, Roczniki Chem. 8, 290-324 (1928).
40. B. Bobrański, Mikrochim. Acta 1956, 1735-1746.
41. R.F. Culmo, Microchem. J. 17, 499-507 (1972).
42. F. Scheidl and V. Toome, Microchem. J. 18, 42-50 (1973).
43. M. Bigois, C. Carriere and P. Linet, Microchem. J. 23, 110-120 (1978).
44. P. Paroutaud, B. Cousin and D. Fraisse, Microchem. J. 25, 267-280 (1980).
45. W.J. Kirsten, Mikrochim. Acta 1976II, 299-310.
46. W. Merz, Mikrochim. Acta 1978II, 519-534.
47. A. Campiglio, Mikrochim. Acta 1983I, 443-455.
48. R. Cassat and M. Pont, Bull. Soc. Chim. France 1972, 1229-1233.
49. B. Griepink, F.G. Römer and W.J. van Oort, Microchem. J. 20, 33-38 (1975).
50. F. Ehrenberger, Z. Anal. Chem. 306, 24-25 (1981).
51. S. Ebel, J. Hocke and B. Rayer, Z. Anal. Chem. 308, 437-440 (1981).
52. B. Kratochvil and C. Maitra, Int. Lab. April 1983, 24-31.
53. A.M.G. Macdonald, Pure and Appl. Chem. 45, 31-37 (1976).
54. W.J. Buis, B. Griepink, L. Haemers, Y. LeDuigou and F. Sels, Mikrochim. Acta 1981I, 39-48.
55. J.T. Clerc and E. Pretsch, Z. Anal. Chem. 305, 124-126 (1981).
56. W. Merz, E. Brodkorb and M. Kranz, Mikrochim. Acta 1972, 939-954.
57. W. Merz, Talanta 21, 481-499 (1974).
58. K. Fenkart, R. Kübler, W. Padowetz, J. Pavel, H. Wagner, D. Hauenstein, G. Michel, R. Werder, R. Landis and H.J. Schrader, Z. Anal. Chem. 282, 177-188 (1976).
59. E. Brodkorb, M. Kranz and H. Scherer, Z. Anal. Chem. 287, 257-263 (1977).
60. P.L.M. van den Bosch, M.H.C. Janssen and H.M. Buck, Mikrochim. Acta 1979II, 85-96.
61. J. Baur and A. Dirscherl, Mikrochim. Acta 1980I, 229-244.
62. G.M. Maciak, R.A. Byers and P.W. Landis, Microchem. J. 18, 8-17 (1973).
63. G.M. Maciak, P.W. Landis and E. Kozłowski, Microchem. J. 24, 64-72 (1979).
64. G.M. Maciak and E. Kozłowski, Microchem. J. 24, 421-425 (1979).
65. E. Kozłowski and G.M. Maciak, Microchem. J. 26, 236-241 (1981).
66. G.M. Maciak, Ph. D. Thesis, Technical University of Gdańsk (1979).
67. W. Merz, Anal. Chim. Acta 53, 429-435 (1971).
68. G.M. Maciak, E. Kozłowski, P. Landis and W. Chrzanowski, 9th International Microchem. Symp., Amsterdam (1983), Abstracts of Papers.
69. A. Campiglio and G. Traverso, Mikrochim. Acta 1980I, 485-494.
70. N.E. Gelman, Pure and Appl. Chem. 44, 493-507 (1975).
71. A. Dirscherl, Mikrochim. Acta 1980I, 307-316.
72. A. Campiglio, Mikrochim. Acta 1982II, 347-361.
73. A. Pietrogranda, G.D. Fini and A. Guerato, Mikrochim. Acta 1983I, 325-328.
74. H. Small, T.S. Stevens and W.C. Bauman, Anal. Chem. 47, 1801-1809 (1975).
75. S. Yonemori and M. Noshiro, Repts. Res. Lab., Asahi Glas Co., Ltd. 31, 17-22 1981 - according to Z. Anal. Chem. 314, 180 (1983).
76. E.L. Johnson, Int. Lab. April (1982), 110-115.
77. G. Dugan, Anal. Lett. 10, 639-657 (1977).

78. E. Pella and B. Colombo, Mikrochim. Acta 1978I, 271-286.
79. W.J. Kirsten, Anal. Chem. 51, 1173-1179 (1979).
80. W.J. Kirsten, Euroanalysis-IV, Helsinki (1981), Abstracts, p. 189.
81. W.J. Kirsten, I.E. Ternrud and G.U. Hesselius, manuscript of paper - private commun. June 1983.
82. E. Häberli, Mikrochim. Acta 1973, 597-606.
83. E. Kozłowski and M. Biziuk, IV Polish Conf. on Analyt. Chem., Warsaw (1974), Summaries of Papers, p. 188.
84. E. Kozłowski and M. Biziuk, Wiadomości Chem. 37, No. 2 (1983) - in print.
85. B. Kobylińska-Mazurek and E. Kozłowski, Mikrochim. Acta 1978I, 137-150.
86. E. Kozłowski and M. Biziuk, Mikrochim. Acta 1979II, 1-17.
87. E. Kozłowski and E. Sieńkowska-Zyskowska, Chem. Anal. 26, 45-55 (1981).
88. E. Kozłowski and M. Biziuk, Mikrochim. Acta 1979II, 19-25.
89. V. Rezl, Mikrochim. Acta 1978I, 493-506.
90. V. Rezl, J. Uhdeová and J. Bursa, Mikrochim. Acta 1979II, 343-348.
91. V. Rezl and A. Burešová, Mikrochim. Acta 1982II, 95-105.
92. K. Tsuji, K. Fujinaga and T. Hara, Bull. Chem. Soc. Japan 50, 2292-2298 (1977).
93. T. Hara, K. Fujinaga and K. Tsuji, Bull. Chem. Soc. Japan 51, 1110-1113 (1978).
94. T. Hara, K. Fujinaga and K. Tsuji, Bull. Chem. Soc. Japan 51, 2951-2956 (1978).
95. T. Hara, K. Fujinaga, K. Tsuji and F. Okui, Bull. Chem. Soc. Japan 51, 3079-3080 (1978).
96. T. Hara, K. Fujinaga, F. Okui and K. Negayama, Sci. Eng. Rev. Doshisha Univ. 21, 241-246 (1981).
97. T. Hara, K. Fujinaga and F. Okui, Bull. Chem. Soc. Japan 53, 951-955 (1980).
98. T. Hara, K. Fujinaga and F. Okui, Bull. Chem. Soc. Japan 53, 1308-1311 (1980).
99. T. Hara, K. Fujinaga and F. Okui, Bull. Chem. Soc. Japan 54, 2956-2959 (1981).
100. T. Hara and F. Okui, Bull. Chem. Soc. Japan 55, 329-330 (1982).
101. T. Hara and F. Okui, Bull. Chem. Soc. Japan 55, 2127-2130 (1982).
102. F. Sels, Mikrochim. Acta 1980II, 245-255.
103. W. Walisch and O. Jaenicke, Talanta 18, 165-173 (1971).
104. W. Walisch and O. Jaenicke, Talanta 22, 167-184 (1975).
105. O. Jaenicke and W. Walisch, Talanta 22, 345-357 (1975).
106. H.C.E. van Leuven, Anal. Chim. Acta 49, 364-366 (1970).
107. H.C.E. van Leuven, Z. Anal. Chem. 264, 220-224 (1973).
108. S.A. Liebman, D.H. Ahlstron, G.D. Pruder, R. Averitt and E.J. Levy, Anal. Chem. 44, 1411-1415 (1972).
109. S.A. Liebman, D.H. Ahlstron, C.D. Nauman, R. Averitt, J.L. Walker and E.J. Levy, Anal. Chem. 45, 1360-1364 (1973).
110. V. Rezl, J. Chromatogr. 251, 35-60 (1982), and references cited therein.
111. L.M. Faires, Int. Lab. April (1983), 14-22.
112. C.A. Bach and D.J. Lisk, Anal. Chem. 39, 786-789 (1967).
113. W.L. Yu, Q.Y. Qu, K.H. Zeng and G.C. Wang, Proceedings on the 4th International Symp. on Capillary Chromatogr., Heidelberg (1981), p. 445-464.
114. S.A. Estes, P.C. Uden and R.M. Barnes, J. Chromatogr. 239, 181-189 (1982).
115. L. Stieglitz and W. Roth, Analytical Techniques in Environmental Chemistry, J. Albaiges, Editor, Pergamon Press, Oxford (1980), p. 345-352, and references cited therein.
116. D.L. Windsor and M.B. Denton, Anal. Chem. 51, 1116-1119 (1979).
117. C.H. Gast, J.C. Kraak, H. Poppe and F.J.M.J. Maessen, J. Chromatogr. 185, 549-561 (1979).
118. D.L. Windsor and M.B. Denton, Appl. Spectrosc. 32, 366-371 (1978).
119. S.K. Hughes, R.M. Brown, Jr. and R.C. Frey, Appl. Spectrosc. 35, 396-400 (1981).
120. H. Kienitz, Z. Anal. Chem. 300, 2-3 (1980).