ОСНОВНІ ПУБЛІКАЦІЇ

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THE APPLICATIONS OF THE GAS CHROMATOGRAPHY WITH ATOMIC EMISSION DETECTION FOR ENVIRONMENTAL POLLUTION ANALYSIS

В обзоре описаны конструкция, методы работы и свойства атомно-эмиссионного детектора и поданы специфические ссылки на результаты анализа загрязнителей окружающей среды. Показано применение детектора в газовой хроматографии при проведении анализа различных загрязнителей окружающей среды. Описываются преимущества детектора, включая его высокую чувствительность, специфичность и возможность определения элементного состава анализируемых соединений.

В огляді описано конструкцію, методи роботи і властивості атомно-емісійного детектора та подано специфічні посилання на результати аналізу забруднювачів навколишнього середовища. Показано застосування детектора в газовій хроматографії під час проведення аналізу різних забруднювачів навколишнього середовища. Описано переваги детектора, включаючи його високу чутливість, специфічність і можливість визначення елементного складу аналізованих сполук.

Introduction

More then 13 million compounds of the total number of chemical compounds which exist in the world have already been characterized by determination of their chemical formulas and principal properties. The direct human surroundings are estimated to contain about 1 million chemical compounds starting with ones occurring at a level of 0.001 ppb. Most of them are organic compounds. The compounds that may be considered either beneficial or indifferent to the human

health, appear to occur in the minority in human surroundings. On the other hand, numerous compounds even if present only in very minute amounts, are well known for their adverse effect on the human body. Therefore, it is advisable to detect, identify and determine more and more chemical compounds at lower and lower concentration levels.

Environmental pollutants have been analyzed in various materials and in various qualitative configurations and quantitative proportions. Quite frequently, small amounts of a substance have to be analyzed in the matrix that renders this analysis difficult. It is in such a complicated system that the analyst has sometimes to analyze substances at levels of about 10 ppb or less. Such a low concentration sometimes lead to an absolute quantity of the compound to be determined as low as 1 picogram that is introduced into an analytical instrument.

The above considerations point out that a good analytical method should enable trace amounts of sample components to be detected, identified and determined. With regard of these requirements it is easy to see that chromatography is the method which answers to these requirements best of all in view of its potential possibilities.

At the moment, chromatography is the most popular method for analyze environmental pollutants. The gas chromatography is the most important chromatographic technique of various existing ones, particularly in the analysis of air. A lot of World (ISO) and European (CEN) Standards have been recommending gas chromatography as analytical tool. The number of such standards directly increase and that is the convincing proof of the importance of the gas chromatography in the analysis of environmental pollutants.

The high importance of gas chromatography as an analytical method is associated with the development of chromatographic detectors and their enhanced selectivity and detection abilities. The instruments that combine the gas chromatograph with a mass-spectrometer – an infrared spectrophotometer or an atomic-emission- spectrometer – becomes more important.

2. The construction, operation mode and properties of the atomic emission detector

The advent of the atomic emission detector (AED) introduced into analytical practice by the Hewlett-Packard Company, has opened new vistas in the potential of the gas chromatography (GC) detection [1, 2]. The GC/AED was the first fully automated instrument, which enabled to detect the analyzed elements while the analyte was being eluted from the chromatographic column [3].

The atomic emission phenomenon has often been used in the chemical analysis. In the simplest case, it has been used to detect metals. A metal compound applied, for example, as a drop of a solution onto a platinum wire and placed in the gas flame, gives the flame the color characteristic of the metal. The color of the

flame is derived from the energy emitted by the metal electrons that have been excited by the supplied thermal energy. Only few elements emit a visible light in the excited condition. Many elements emit the light in the ultraviolet range.

The AED responds to the type and to the quantity of energy emitted by atoms of various elements, after these atoms have been excited by the energy supplied in a helium gas plasma. The atoms of the elements, which appear at the high plasma temperature as a result of the decomposition of the compounds eluted from a chromatographic column, emit the light at a wavelength characteristic of a given element.

Thus, the AED enables to identify the elements which constitute analyzed and eluted from the chromatographic column compounds. The simultaneous measurement of the emitted light intensity allows to determine the contents of the individual elements in the analyzed compounds. The AED is specific towards the element whose emitted light has been recorded.

The scheme of gas chromatographic atomic emission detector is shown in Fig.1.

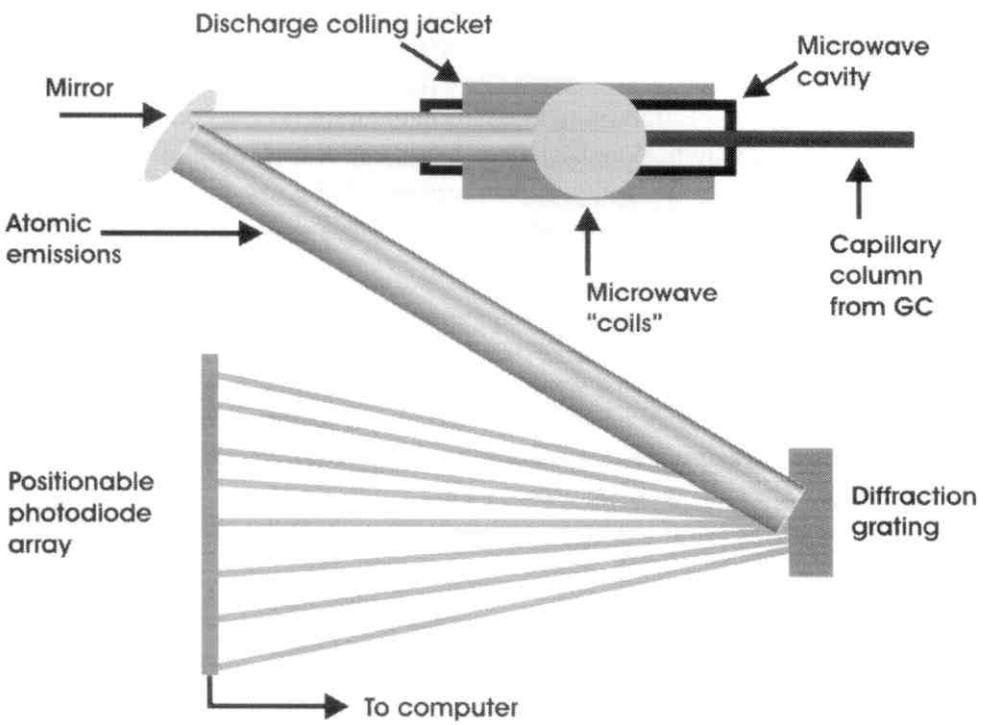

Fig. 1. **The scheme of gas chromatographic atomic emission detector**

The components of a sample isolated in the chromatographic column are introduced into the microwave-induced helium gas plasma at temperatures of 3 000–10 000 K at a pressure close to atmospheric pressure [1].

Plasma is generated from helium gas, which is used as a carrier gas in the chromatographic column. Therefore, helium is the only carrier gas that should be used. To enhance the detector's efficiency, small amounts of reactive gases, hydrogen or oxygen, are added to the helium gas past the column and prior to the detector. In the plasma the chromatographic compounds are decomposed into atoms.

The light emitted by the excited atoms is detected by photodiodes, which are laid in an immobile matrix and respond to the light of a well-defined wavelength. In the photodiodes the energy of the light is converted into electric signals, which are registered by a computer. The characteristic wavelength of the light emitted by the element enables to identify the element. Perfect resolution of all the components is not required, because the individual elements are detected very selectively – even in the case of overlapping peaks.

In this way several elements can be detected simultaneously. Emission spectra [4] of the elements which can be recorded within the range 171–690 nm enable to identify the detected elements reliably.

The AED enables to detect practically all the elements encountered in volatile organic compounds with good selectivity. The following elements and their stable isotopes can be detected: carbon, nitrogen, oxygen, bromine, chlorine, fluorine, iodine, phosphorus, silicon, sulfur, carbon-13, nitrogen-15, deuterium, arsenic, iron, lead, mercury, nickel, selenium, tin, and vanadium.

The AED detect carbon better than the flame-ionization detector, which is generally used in the GC analysis of hydrocarbons. The AED can detect halogens with sensitivity close to sensitivity of the electron-capture detector, which is known to be the best detector to detect halogens. At the same time, the AED is less sensitive to the contaminants occurring in a given sample than the electron-capture detector but it differentiates fluorine, chlorine, bromine and iodine. Most elements can be detected at concentrations of several to several score of pg/s. Oxygen is detected not so well as other elements, *ca.* 50 pg/s, but other detectors are still less sensitive than AED. Oxygen is generally difficult to detect [5].

In quantitative analysis use is based on the fact that the height of the chromatographic peak is proportional to the concentration of the element (intensity of emitted light) contained in the chromatographed compound.

The standard used in the quantitative analysis does not need to be identical with the substance determined. The standard may be a different substance but should be a substance containing a well-known amount of the element to be determined. The calibration curve to be used in the absolute calibration technique can be ascertained by chromatographying under identical conditions a mixture of compounds containing several compounds with different amounts of the element to be determined. This is quite convenient especially when the standard is very expensive or difficult to achieve. Peak height measurements and calculations can be automated.

Results of the qualitative and quantitative analyses can be used to establish the empirical formula of the components of the analyzed sample and to identify the components of the analyzed mixture [6].

3. Examples of applications of the atomic emission detector to the analysis of environmental contaminants

The atomic emission detector was introduced into analytical laboratories only a decade and so ago and since then has found numerous applications because of its high sensitivity, specificity and possibility of identifying the elemental composition of the analyzed substances. It has been used in chemical, petrochemical, pharmaceutical, cosmetic and foodstuff industries.

Analyses of drugs [7], polymer additives [8], metal porphyrins and other organometal compounds in crude oil [9], and polychlorinated biphenyls in food products [10] have been reported. GC/AED is especially useful for analysis compounds containing heteroatoms in molecules, e.g. for coal light distillates and its hydrotreated oil [11].

N-containing components of humic and fulvic acids were determined using pyrolysis gas chromatography atomic emission detector [12]. Pyrolysis gas chromatography coupled with atomic emission spectrometry is useful for analysis sewage sludges of different origins [13].

The properties of the AED make it particularly useful for the analysis of environmental pollutants. It has been used to analyze pollutants in air, water, soil and in various sediments [14–16].

It allows to analyse, for example, freons [17]. The detection limits of several fluorocarbons in air depend on the kind of a fluorocarbon.

Purge-and-trap capillary gas chromatography with atomic emission detection for volatile halogenated organic compounds was used for the determination of volatile halogenated organic compounds in waters and beverages [18] – Fig. 2.

Purge-and-trap enrichment coupled to GC/AED was used for the determination of methyl tert – butyl ether and tert – butyl alcohol in seawater samples [19]. The rapid screening of volatile chlorinated compounds in water was performed using GC/AED coupled with solid phase microextraction [20]. The wide-range automated screening of over 400 industrial, agrochemical and household microcontaminants in surface water by GC/AED/MS was performed using semipermeable membrane devices and solid-phase extraction [21].

An important area of AED's application is the analysis of pesticides belonging to different groups [22–25]. Pesticides are encountered in environmental samples and they usually occur at low concentrations and in the presence of interfering substances. Therefore, it is important to identify elements in the individual components of the sample.

On the other hand, pesticides are well-suited for the AED analysis because their molecules contain numerous hetero-atoms and the AED detect them easily.

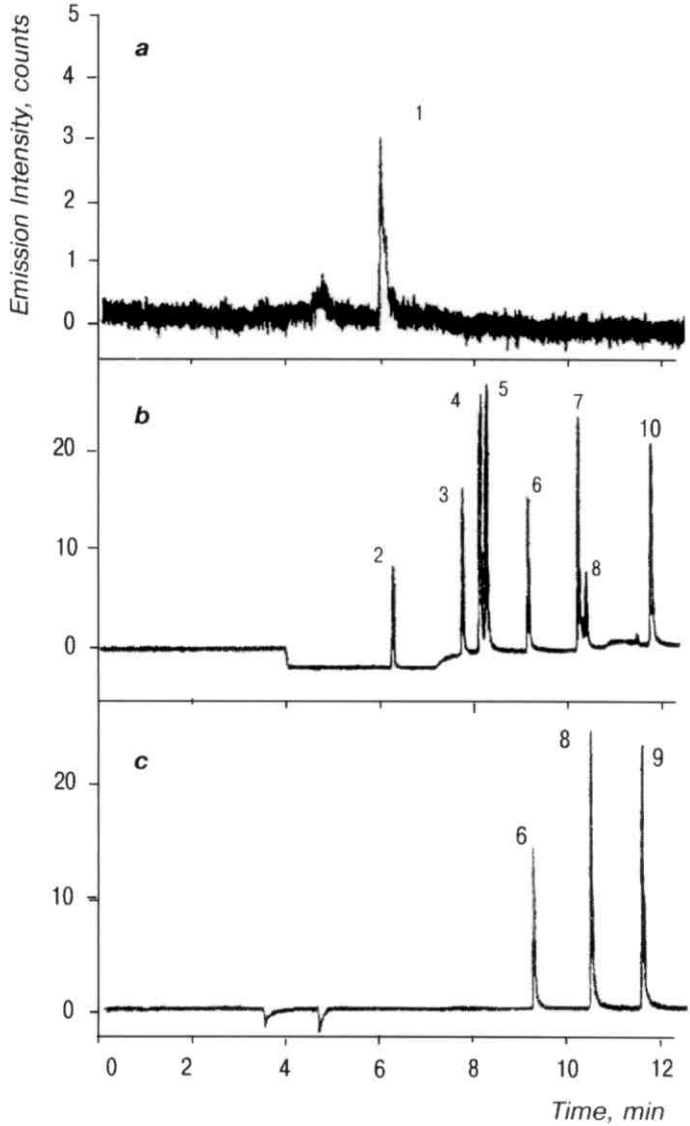

Fig. 2. **GC–AED chromatograms mixture of the volatile organic compounds: *a* – *I* (193 nm), *b* – *Cl* (479 nm), *c* – *Br* (478 nm)**

Concentrations of the standard mixture:

1 – iodomethane, 10 μg/dm^3 ; *2* – dichloromethane, 20 μg/dm^3; *3* – chloroform, 3 μg/dm^3;
4 – tetrachloromethane, 18 μg/dm^3; *5* – 1,2-dichloroethane, 4 μg/dm^3;
6 – bromodichloromethane, 7 μg/dm^3; *7* – tetrachloroethene, 10 μg/dm^3;
8 – dibromochloromethane, 4 μg/dm^3; *9* – bromoform, 4 μg/dm^3;
10 – 1,1,2,2-tetrachloroethane, 5 μg/dm^3

The hetero-atoms are encountered in pesticides in the following ascending order of occurrence: I < Br < F < P < S < Cl < N < O. These hetero-atoms can be identified easily. It should be emphasized that here the AED replaces several spe-

cific detectors, *e.g.*, ECD, NPD and FPD. However, those detectors can hardly be used to determine the individual elements but those detectors can not identify the type of the halogen which is the component of the pesticide, especially in the case of the electron-capture detector (ECD).

It has been shown that the AED can identify chemical compounds, which occur in the sample at the level of a few nanograms and contain up to seven elements. Analysis of 10-mL river and tap water samples by the use of solid-liquid extraction, showed organophosphorus pesticides to be detectable to within 0.1 μg/L. Microextraction techniques allowed to attain the limit of 0,5–3 μg/L.

Generally, the extraction procedures used to prepare samples plus the AED detection technique allow to analyze various groups of pesticides which occur in water at the level of ppb, that is lower than the permissible levels. In addition to the analysis in water, pesticides have been analyzed in strawberry, carrot, apple, horse-radish, potato, onion and rice.

An example of pesticides chromatogram is given in Fig.3.

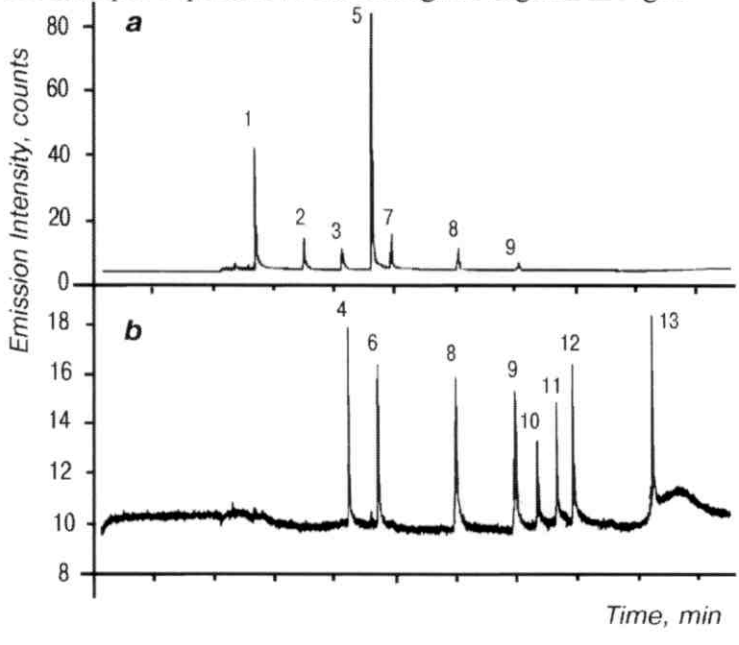

Fig. 3. **GC–AED chromatograms of mixture of pesticides by element wavelength: *a* – S (181 nm), *b* – Cl (479) nm**

1 – Methamidophos (600 ng/ml); *2* – acephate (550 ng/ml); *3* – omethoate (600 ng/ml); *4* – chlorpropham (250 ng/ml); *5* – dimethoate (550 ng ml); *6* – lindane (50 ng/ml); *7*– diazinon (190 ng ml); *8* – chlorpyriphos (200 ng/ml); *9* – α-endosulfan (110 ng/ml); *10* – *p, p*-DDE (60 ng/ml); *11*– *p, p*-DDD (60 ng ml); 12 – *p, p*-DDT (100 ng/ml); *13*– permethrin (200 ng/ml)

The AED has been used to analyze various organic compounds including polychlorinated biphenyls in sewage and water sediment extracts [26, 27]. It was found out that the sediments contain chlorotoluene, benzaldehyde, 1,4-dichlor-

obenzene, nitrobenzene, trichlorobenzene and chlorobenzyl chloride.The gas chromatograph coupled with the AED was used to analyze coal pyrolyzates, which contain nitrogen and sulfur and 2-picoline oxidates formed in moist air [11, 26].

Environment protection aspects make the determination of sulfur compounds in liquid fuels a matter of importance, both in crude oil and in various gasoline grades. The AED has proved its use for this purpose [28–31] – Fig. 4.

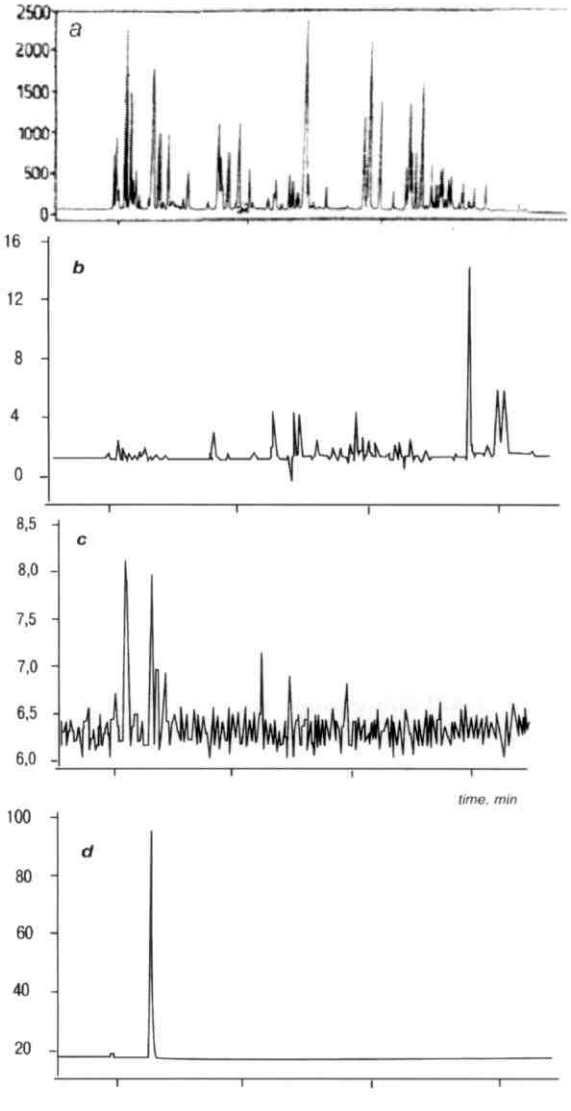

Fig. 4. **The chromatograms of unlead petrol from CPN fuel station:**

a – carbon chromatogram, *b* – sulphur chromatogram,
c – lead chromatogram, *d* – oxygen chromatogram

It can be successfully used for analysis of sulfur compounds in natural gases (*e. g.* in earth gas) and in edible oils. Comprehensive two-dimensional gas chromatography with atomic emission detection is particularly useful in petrochemical analysis [32]. In addition to sulfur compounds, oxygen-containing compounds can be detected. This possibility is particularly important in the case of gasolines in which the large number and high proportion of hydrocarbons can render the separation of compounds, which contain sulfur, oxygen and nitrogen and thus their analysis by gas chromatography using conventional detectors is difficult.

The AED makes detection of nitrogen compounds very easy in crude oil and petrochemicals.

During the recent decades the number of applications of organotin compounds as polymer stabilizers, pesticides and herbicides increased [33]. Their use results in contamination of the environment. Accumulation of these substances in aquatic sediments and organisms has been reported. Their toxicity is related to their chemical structure (*e. g.*, to the number of alkyl groups in the molecule) and thus it is not only important to detect the presence of tin in a molecule but also to establish the structure of the compound (s) in which it occurs.

The organotin compounds are volatile enough to be analyzed by gas chromatography. The Hewlett-Packard instrument allows to chromatograph compounds at temperatures up to 450 °C and then operated in conjunction with the AED gives very good results [33]. Capillary gas chromatography coupled with atomic emission detection allows to determine organotin compounds at the level of a few ppb.

Similarly as organotin compounds, the organomercury compounds which occur in biological (e.g. in fish tissues) and environmental samples can be analyzed with the aid of AED [34–36]. These compounds are used as fungicides or else are formed from inorganic mercury compounds as a result of interaction with river microorganisms.

In the case of organometal compounds GC/AED can determine volatile organolead compounds, e. g. tetraethyllead and organomercury compounds [37].

The organometallic forms of mercury, tin and lead were analysed performing in situ derivatization and trapping [38]. Aqueous derivatization of organomercury with sodium tetraethylborate and sodium tetraphenylborate may be useful prior to GC/AED determination [37].

Atoms of the same metal, which present in the sample at various oxidation degrees produce identical emission spectra and therefore the GC/AED analysis is not speciation. However, if atoms of the metal which occur at different oxidation degrees can be separated in the GC column, speciation can be carried out [34, 36].

The GC/AED can be applied to special analysis of environmental contaminants like chemical warfare agents [24].

This technique has been used to analyze the sulfur mustard packages raised from the Baltic sea [39] – Fig. 5.

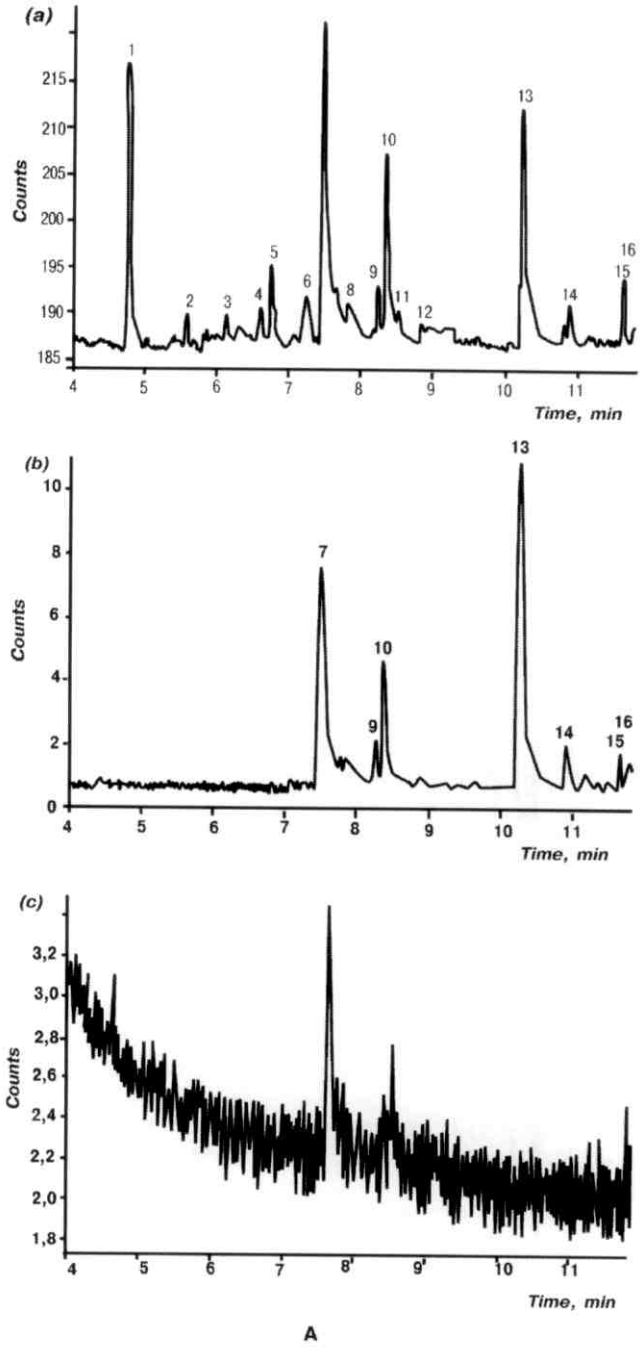

Fig. 5 A. **The first part of the element chromatograms of a sample of the yperite block obtained by GC–AED on channel:**

a – carbon (C) – 193 nm; *b* – sulphur (S) –181 nm; *c* – chlorine (Cl) – 479 nm; split ratio 20:1

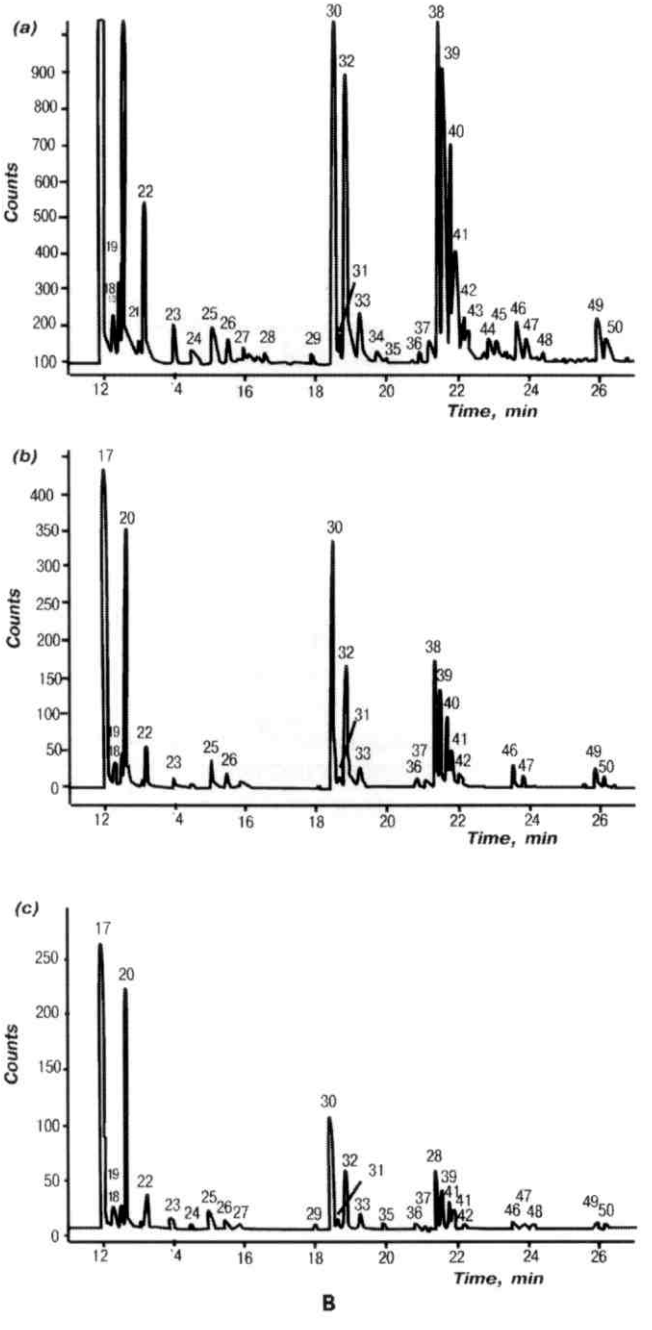

Fig. 5 B. **The second part of the element chromatograms of a sample of the yperite block obtained by GC–AED on channel:**

a – carbon (C) – 193 nm; *b* – sulphur (S) –181 nm; *c* – chlorine (Cl) –479 nm; split ratio 60:1

The GC/AED technique is one of the best techniques recently introduced into the chemical analytical laboratory. In the analysis of environmental samples, the AED can perform the functions of several conventional GC detectors. The chromatograms recorded with AED, and specific as regards elements, allow to collect more accurate information about the composition of the analyte than even those which recordered with several conventional detectors and the AED works faster.

The GC/AED chromatograph may be the only chromatograph used in an analytical laboratory but it is better when a gas chromatograph coupled with a mass spectrometer [24, 40] is also available. Neither the mass spectrometer nor the FTIR spectrophotometer enable the simultaneous qualitative and quantitative analysis of several elements. Therefore it may happen that the identification of a chemical compound achieved by the simultaneous use of IR spectrophotometry and mass spectrometry are inconsistent. Then, the AED will allow to confirm the information afforded by either the MS or the IR instrument and to obtain correct identification. GC/MS, GC/AED and nuclear magnetic resonance together were used for identification of pharmaceutically related impurities with unknown structures [41]. GC/MS, GC/AED and GC/FTIR were applied as complementary analytical techniques for the identification of unknown impurities in pharmaceutical analysis [42].

References

1. ***B. D. Quimby, J. J. Sullivan***, Anal. Chem., 62 (1990) 1027.
2. ***L. L. P. van Stee, U. A. Th. Brinkman***, Tr. Anal. Chem., 21(2002) 618.
3. ***R. L. Firor***, American Laboratory, 21 (1989) 113.
4. ***J. J. Sullivan***, Trends in Anal. Chem., 10 (1991) 24.
5. ***B. Bradley, J. W. Carnahan***, Anal. Chem., 60 (1988) 858.
6. ***W. Schäfer***, J. High Resolut. Chromatogr., 16 (1993) 674.
7. ***B. D. Quimby, P. C. Dryden, J. J. Sullivan***, Anal. Chem., 62 (1990) 2509.
8. ***F. David, P. Sandra***, LC-GC Int., 5 nr 12, (1992) 22.
9. ***Y. Zeng, J.A. Seeley, T. M. Dowling, P. C. Uden, M. Y. Khuhawar***, J. High Resolut. Chromatogr., 15 (1992) 669.
10. ***F. E. Ahmed***, Trends Anal. Chem., 22 (2003) 170.
11. ***S.D.S. Murti, K. Sakanishi, O. Okuma, Y. Korai, I. Mochida***, Fuel, 81 (2002) 2241.
12. ***X. Song, S.O. Farwell***, J. Anal. Appl. Pyrolysis, 71 (2004) 901.
13. ***E. Jarde, F. Vilmin, L. Mansuy, P. Faure,*** *J. Anal. Appl. Pyrolysis,* 71 (2004) 553.
14. ***H. Frischenschlager, C. Mittermayr, M. Peck, E. Rosenberg, M. Grasserbauer***, Fresenius' J. Anal. Chem. 359 (1997) 213.
15. ***P. Viñas, N. Campillo, I. López-García, N. Aguinaga, M. Hernández-Córdoba***, J. Chromatogr. A, 978 (2002) 249
16. ***N. Campillo, P. Viñas, I. López-García, N. Aguinaga, M. Hernández-Córdoba***, Talanta, 64 (2004) 584.
17. ***S. R. Sousa, S. E. Bialkowski***, Anal. Chim. Acta, 433 (2001) 181.
18. ***N. Campillo, P. Viñas, I. López-García, N. Aguinaga, M. Hernández-Córdoba***, J. Chromatography A, 1035 (2004) 1.

19. ***M. Mezcua, A. Aguera, M.D. Hernando, L. Piedra, A.R. Fernández-Alba***, J. Chromatogr. A, 999 (2003) 81.

20. ***S. I. Semb, S. Pedersen-Bjergaard, E. M. Brevik,*** Chemosphere, 49 (2002) 1349.

21. ***L. L. P. van Stee, P. E. G. Leonards, W. M. G. M. van Loon, A. J. Hendriks, J. L. Maas, J. Struijs, U. A. Th. Brinkman***, Water Res., 36 (2002) 4455.

22. ***J. L. Bernal, M. J. del Nozal, M. T. Martin, J. J. Jimenez***, J. Chromatogr. *A*, 754 (1996) 245.

23. ***X. Quan, S. Chen, B. Platzer, J. Chen, M. Gfrerer***, Spectrochim. Acta, B 57 (2002) 189.

24. ***L. L. P. van Stee, U. A. Th. Brinkman***, Trends Anal. Chem., 21 (2002) 618.

25. ***L. L. P. van Stee, P. E. G. Leonards, R. J. J. Vreuls, U. A. Th. Brinkman,*** Analyst, 124 (1999) 1547.

26. ***M. Cooke, D. A. Leathard, C. Webster, V. Rogerson***, J. High Resolut. Chromatogr., 16 (1993) 660.

27. ***P. Faure, F. Vilmin, R. Michels, E. Jarde, L. Mansuy, M. Elie, P. Landais***, J. Anal. Appl. Pyrol., 62 (2002) 297.

28. ***A. Stumpf, K. Tolvaj, M.*** **Juhasz**, J. Chromatogr., A 819 (1998) 67.

29. ***S. G. Mössner, S. A. Wise***, Anal. Chem. 71 (1999).

30. ***A. H. Hegazi, J. T. Andersson, M. Sh. El-Gayar***, Fuel Proces. Technol., 85 (2003) 1.

31. ***Z. Witkiewicz, S. Popiel***, Przem. Chem., 79 (2000) 123.

32. ***L. L. P. van Stee, J. Beens, R. J. J. Vreuls, U. A. Th. Brinkman,*** J. Chromatogr. A, 1019 (2003) 89.

33. ***Yan Liu, V. Lopez-Avila, M. Alcaraz, W. F. Bechert***, J. High Resolut. Chromatogr., 16 (1993) 106.

34. ***C. Dietz, Y. Madrid, C. Cámara, P. Quevauviller, J. Anal. Atom. Spectrom.***, 14 (1999) 1349.

35. ***J. Sanz, A. de Diego, J. C. Raposo, J. M. Madariaga***, Anal. Chim. Acta, 486 (2003) 255.

36. ***J.S. Landaluze, A. de Diego, J. C. Raposo, J. M. Madariaga***, Anal. Chim. Acta, 508 (2004) 107.

37. ***Y. Cai , S. Monsalud , R. Jaffe , R. D. Jones***, J. Chromatogr. *A*, 876 (2000) 147.

38. ***R. Reuthera, L. Jaegera, B. Allard***, Anal. Chim. Acta, 394 (1999) 259.

39. ***M. Mazurek, Z. Witkiewicz, S. Popiel, M. Śliwakowski,*** J. Chromatogr. A, 919 (2001) 133.

40. ***F. David, P. Sandra***, J. High Resolut. Chromatogr., 14 (1991) 554.

41. ***K. Łaniewski, Malin Vågerö, E. Forsberg, T. Forngren, G. Hagman***, J. Chromatogr. A, 1027 (2004) 93.

42. ***K. Łaniewski , T. Wannman, G. Hagman***, J. Chromatogr. A, 985 (2003) 275

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