Short communication

Increasing the accuracy of determination of n_C/n_H ratios by gas chromatography–atomic emission detection

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Abstract

The influence of oxygen content in helium on the accuracy of n_C/n_H ratio determination for model mixtures of aliphatic and polyaromatic hydrocarbons and polychlorinated biphenyls was studied. The best accuracy was achieved at the oxygen content ca. 9%, which was the maximal possible oxygen content in helium for this GC–atomic emission detection (helium flow rate was 25 ml min^{-1}). Using the maximal oxygen flow in plasma the n_C/n_H ratio determination accuracy improvement was accompanied by 10-fold increase in detection limit.
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Keywords: Gas chromatography-atomic emission detection; n_C/n_H ratios; Aliphatic hydrocarbons

1. Introduction

The developing of empirical formulae determination method is one of the possible ways to improve the reliability of identification of unknowns. From this viewpoint, attractive is gas chromatography with atomic emission detection, because, providing full atomization of analytes, the atomic emission detection (AED) signal should be independent of their structures. Therefore, empirical formulae could be determined using only one mixture component as a reference for other components.

In the large majority of publications it has been shown that the AED response is dependent on analyte structure and concentration and plasma conditions [1–4]. The requirement of accurate determination of elemental ratios is that the reference compound has a structure, retention time, concentration and elemental composition similar to compound being determined [2,5–7]. However, instrumental parameters influencing the accuracy of elemental ratio determination by GC–AED have not been thoroughly investigated, and usually the instrument is operated at gas pressures recommended by manufacturer without indication of the respective flow rates.

The GC–AED system developed by Hewlett-Packard is most widely used nowadays. In order to improve the chromatographic peaks shape, increase the plasma electron density and prevent carbon deposition on discharge tube walls, such reagent gases as oxygen, hydrogen, and/or nitrogen–methane (9:1) mixture are added to the helium plasma, depending on element wavelengths to be registered [8,9]. Oxygen is used as a reagent gas for simultaneous C and H element chromatograms registration.

Thus, we have decided to study the influence of oxygen content in helium on the accuracy of n_C/n_H ratio determination for model mixtures of aliphatic and polyaromatic hydrocarbons and polychlorinated biphenyls. n_C/n_H ratios were determined for all model compounds using tridecane as a reference compound.

2. Experimental

2.1. Chemicals

Undecane, dodecane, tridecane, tetradecane, pentadecane, and hexadecane were purchased from Aldrich (Milwaukee,

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WI, USA). Naphthalene ($C_{10}H_8$), acenaphthene ($C_{12}H_{10}$), fluorene ($C_{13}H_{10}$), pyrene ($C_{16}H_{10}$), and chrysene ($C_{18}H_{12}$) were purchased as 2×10^{-4} g/μl solutions in acetonitrile from Ecros (St. Petersburg, Russia). 2-Chlorobiphenyl, 2,3-dichlorobiphenyl, 2,4,5-trichlorobiphenyl, and 2,2′,4,4′-tetrachlorobiphenyl were purchased as 1×10^{-7} g/μl mixture in acetone from Ultra Scientific (North Kingstown, RI, USA). Hexane, acetonitrile and acetone were supplied from Lecbiopharm (Moscow, Russia).

Helium (99.9999%), nitrogen (99.99%), oxygen (99.999%), hydrogen (99.9999%), and nitrogen/methane mixture (9:1) (99.99%) were obtained from PromGasService (Moscow, Russia).

The stock solutions containing 5×10^{-5} g/μl per individual hydrocarbon were prepared by dissolving 50 mg of each hydrocarbon in 1 ml of n-hexane. The model mixtures were prepared by dilution and/or mixing of the stock solutions.

The model mixtures of polyaromatic hydrocarbons and polychlorinated biphenyls were prepared in acetone and acetonitrile, respectively. Tridecane was added as an internal standard.

2.2. GC–AED

A microwave-induced plasma atomic emission detector, model "G2350A" (Agilent, Waldbronn, Germany), was coupled to a "6890N" gas chromatograph. The GC was equipped with a "7683" automatic sampler and a split–splitless capillary injection port. For instrument control and operation G2370AA Chemstation with the G2360AA GC–AED software was used. Chromatographic separation was performed on a 25 m × 0.32 mm i.d. HP-1 100% polydimethylsiloxane capillary column (Agilent) with 0.17 μm film thickness. Sample volumes of 1 μl were injected by a 10 μl syringe of the automatic sampler in splitless mode (injection port temperature 280 °C). The flow rate of carrier gas (helium) was 1.5 ml min^{-1}. Model compounds were fully separated applying temperature programming. Following injection, the solvent was vented for 4 min. The transfer line and detector cavity were operated at 280 °C. Carbon and hydrogen were registered at 496 and 486 nm, respectively. Oxygen was used as a reagent gas. The helium and oxygen flow rates through the plasma were calculated using the flow rate values measured at the vent lines of the AED system by a bubble meter at different oxygen pressures. The range of oxygen flow rates we investigated was 0–2.5 ml min^{-1} (corresponded to pressures 0–6.89 bar). The oxygen pressure at the recommended by the manufacturer instrument operation mode was 1.01 bar, the corresponding oxygen content in plasma was ca. 1.5%.

3. Results and discussion

Providing the independence of detector C and H responses on structure of the analytes, n_C/n_H ratio can be calculated for unknown compound by use of the equation:

$$\frac{n_{C,unknown}}{n_{H,unknown}} = \frac{S_{C,unknown}}{S_{H,unknown}} \frac{n_{C,reference}}{n_{H,reference}} \frac{S_{H,reference}}{S_{C,reference}},$$

where $n_{C,unknown}/n_{H,unknown}$ and $n_{C,reference}/n_{H,reference}$ are the ratios of the numbers of C and H atoms in the molecule of unknown and reference compound, respectively; $S_{C,unknown}/S_{H,unknown}$ and $S_{H,reference}/S_{C,reference}$ are the ratios of peak areas registered on C and H channels for unknown and reference compound, respectively.

The relative errors of calculated n_C/n_H ratios can be evaluated as:

$$\Delta\,(\%) = \frac{|(n_{C,calc.}/n_{H,calc.}) - (n_{C,real}/n_{H,real})|}{n_{C,real}/n_{H,real}} \times 100\%,$$

where $n_{C,real}/n_{H,real}$ and $n_{C,calc.}/n_{H,calc.}$ are real and calculated n_C/n_H ratios, respectively.

3.1. n_C/n_H ratio determination for model aliphatic hydrocarbons

We have studied the accuracy of n_C/n_H ratio determination for the mixtures containing 5×10^{-7}, 1×10^{-7}, 5×10^{-8}, 1×10^{-8}, 5×10^{-7}, and 5×10^{-9} g/μl per component of aliphatic hydrocarbons C_{11}-C_{16}, using tridecane as a reference for other components, and found that the AED response was independent on compound structure, when oxygen content in helium was equal to 1.5% (which was set according to manufacturer recommendations; hereinafter we will name it as "standard oxygen content"). As an example, the results of n_C/n_H ratio determination at the standard oxygen content in helium are given in Table 1 (the concentration of C_{11}–C_{16} hydrocarbons was 5×10^{-7} g/μl).

As it is seen from Table 1, in the standard instrument operation mode no significant n_C/n_H ratio determination accuracy dependence on structure of C_{11}–C_{16} hydrocarbons was observed.

Table 1

Aliphatic hydrocarbons n_C/n_H ratio determination results at the standard oxygen content in helium (1.5%) ($n = 5$, $P = 0.95$; components concentration 5×10^{-7} g/μl)

Oxygen content	Compound	$n_{C,real}/n_{H,real}$	$n_{C,calc.}/n_{H,calc.}$	R.S.D. (%)	Δ (%)
ca. 1.5% (recommended)	$C_{11}H_{24}$	0.46	0.46	0.2	0
	$C_{12}H_{26}$	0.46	0.46	0.1	0
	$C_{13}H_{28}$	0.46	Reference	–	–
	$C_{14}H_{30}$	0.47	0.47	0.1	0
	$C_{15}H_{32}$	0.47	0.47	0.3	0
	$C_{16}H_{34}$	0.47	0.47	0.2	0

Table 2
Polyaromatic hydrocarbons n_C/n_H ratio determination results at the standard and maximal oxygen content in helium using tridecane as a reference compound ($n = 3$, $P = 0.95$; components concentration 2×10^{-8} g/µl)

Oxygen content	Compound	$n_{C,real}/n_{H,real}$	$n_{C,calc.}/n_{H,calc.}$	R.S.D. (%)	Δ (%)
ca. 1.5% (recommended)	$C_{10}H_8$	1.25	1.30	0.3	4
	$C_{13}H_{28}$	0.46	Reference	–	–
	$C_{12}H_{10}$	1.20	1.27	0.4	6
	$C_{13}H_{10}$	1.30	1.37	1.6	6
	$C_{16}H_{10}$	1.60	1.76	0.9	10
	$C_{18}H_{12}$	1.50	1.62	1.5	8
ca. 9% (maximal)	$C_{10}H_8$	1.25	1.23	0.7	2
	$C_{13}H_{28}$	0.46	Reference	–	–
	$C_{12}H_{10}$	1.20	1.17	1.7	3
	$C_{13}H_{10}$	1.30	1.28	0.9	2
	$C_{16}H_{10}$	1.60	1.55	1.6	3
	$C_{18}H_{12}$	1.50	1.48	0.2	1

Table 3
Polychlorinated biphenyls n_C/n_H ratio determination results at the standard and maximal oxygen content in helium using tridecane as a reference compound ($n = 3$, $P = 0.95$; components concentration 2×10^{-8} g/µl)

Oxygen content	Compound	$n_{C,real}/n_{H,real}$	$n_{C,calc.}/n_{H,calc.}$	R.S.D. (%)	Δ (%)
ca. 1.5% (recommended)	$C_{13}H_{28}$	0.46	Reference	–	–
	$C_{12}H_9Cl$	1.33	1.55	1.2	17
	$C_{12}H_8Cl_2$	1.50	1.69	0.9	13
	$C_{12}H_7Cl_3$	1.71	1.99	2.5	16
	$C_{12}H_6Cl_4$	2.00	2.27	2.5	14
ca. 9% (maximal)	$C_{13}H_{28}$	0.46	Reference	–	–
	$C_{12}H_9Cl$	1.33	1.33	1.6	0
	$C_{12}H_8Cl_2$	1.50	1.45	3.0	3
	$C_{12}H_7Cl_3$	1.71	1.68	1.3	2
	$C_{12}H_6Cl_4$	2.00	2.02	0.3	1

3.2. n_C/n_H ratio determination for model polyaromatic hydrocarbons and polychlorinated biphenyls

Aliphatic hydrocarbon response independence on analyte and reference structure, observed by us, should not be considered as an evidence of AED response structure independence for all classes of compounds, because the model hydrocarbons we investigated had very similar structures and n_C/n_H ratios. It has already been shown, that n_C/n_H ratios of such aliphatic compounds as *n*-hexane, cyclohexane, isooctane, *n*-nonane, *n*-dodecane, and *n*-pentadecane could be determined correctly using *n*-octane as a reference compound, whereas n_C/n_H ratios of polyaromatic compounds (benzene, ethylbenzene, *p*-xylene, biphenyl) could not be accurately determined using the same reference compound [4]. As an explanation of this phenomenon, a relatively low hydrogen atom yield during thermal degradation in the plasma as a result of the larger dissociation energy needed for aromatic C−H bonds compared with aliphatic C−H bonds was suggested.

As a possible way to increase the rate of compounds destruction in plasma, we decided to increase the oxidative ability of plasma by using higher oxygen content in helium. In order to study the possibility of obtaining AED response independent on compound structure, and, consequently, of n_C/n_H

determination accuracy improvement at the maximal oxygen content in helium, we used tridecane as an internal standard (reference compound) in the mixtures of polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). The results of n_C/n_H ratio determination at the standard and maximal oxygen content in helium for PAHs and PCBs are given in Tables 2 and 3, respectively. The concentration of components in these mixtures was the same and equal to 2×10^{-8} g/µl.

As can be seen from Tables 2 and 3, using the maximal oxygen content in plasma, the relative error of n_C/n_H ratio determination was 0–3% (instead of 4–17%—using the standard oxygen content), and the AED response became a more structure independent. The other interesting observation is that n_C/n_H ratio determination results, obtained using the standard oxygen content, are overrated, which could be due to the understated hydrogen response. However, this question requires carrying out further investigations.

3.3. Detection limits dependence on oxygen content in helium

When the oxygen content in helium increased from 1.5 to 9%, we observed the detection limits increase by about two

to five times for C and by about three to eight times for H, depending on the compound. As peak areas registered on C and H channels are both necessary for n_C/n_H ratio calculation, the relative n_C/n_H ratio determination accuracy improvement is achieved at the expense of about one order of magnitude detection limit increase (per compound).

4. Conclusion

As a result of our research it has been shown by the example of model PAHs and PCBs with tridecane used as an internal standard, that it was possible to increase the accuracy of n_C/n_H ratio determination thanks to using of higher oxygen concentration in helium, compared to that recommended by the GC–AED manufacturer. The limitation of such approach is compound detection limit increase by about one order of magnitude.

Acknowledgement

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