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Automation of data processing and calculation of retention parameters and thermodynamic data for gas chromatography

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Abstract. The analyses of automation patterns is performed and the programming solution for the automation of data processing of the chromatographic data and their further information storage with a help of a software package, Mathcad and MS Excel spreadsheets, is developed. The offered approach concedes the ability of data processing algorithm modification and does not require any programming experts participation. The approach provides making a measurement of the given time and retention volumes, specific retention volumes, a measurement of differential molar free adsorption energy, and a measurement of partial molar solution enthalpies and isosteric heats of adsorption. The developed solution is focused on the appliance in a small research group and is tested on the series of some new gas chromatography sorbents. More than 20 analytes were submitted to calculation of retention parameters and thermodynamic sorption quantities. The received data are provided in the form accessible to comparative analysis, and they are able to find sorbing agents with the most profitable properties to solve some concrete analytic issues.

1. Introduction

Despite the considerable progress in the hardware implementation of gas chromatography analyses, the software solutions in the field of chromatography processing data are slightly limited in appliance nowadays [1]. Many kinds of both foreign and native software solutions for gas chromatography data processing are known ('Chemstation', 'Multichrom', 'Kristall' etc.).

However, most of them do not correspond to the needs of investigators in full. This happens due to the variety of real analytic issues and their specificity of decision calculations. In particular, the main issue of such kind of software solution is the automation of performance of the quantitative chromatographic analysis, while for the characteristic of new chromatographic materials, the specific algorithm series for the processing of analytes retention parameters is needed, and the calculation of the range of volumes on their basis is required. Thus, the sorbent`s polarity and selectivity investigation is complicated by the existence of various approaches of these concepts definition [2-4]. In this regard, the investigator faces the need to modify methods of experimental data processing, and hence the necessity of programming modification in calculation methods is clear.

2. Chromatographic data operations

2.1. Chromatographic data acquisition

The investigation of chromatographic sorbents` properties was conducted on the gas chromatograph 'MAESTRO 7820' (Agilent Technologies). The device is equipped with a flame-ionization detector and an injection port for packed columns with an electronic gas flow/pressure control. The data acquisition was performed at temperatures of 150, 170, 200°C and with a carrier gas speed (helium) of 30 ml\min. Detector's signals were processed with a help of software solution ChemStation. The further experimental data processing was conducted in compliance with the given method.

2.1. Experiential data processing

The experiential data processing was conducted in compliance with the given method. The adjusted retention time (t'_R) is determined from the formula [11]:

$$t'_R = t_R - t_M \, ,$$

where t_R - retention time; t_M – time of inert compound being in the chromatographic system, min, in the function of which methane was used.

The adjusted retention volume (corrected retention volume V'_r [11]:

$$V'_R = (t_R - t_M)F_C = V_R - V_M \, ,$$

where F_C – volume velocity of a carrier gas, ml/min.

According to the next formula, the Kovach's retention indexes were calculated and then they were used as the relative retention parameters, which do not depend on little accidental fluctuations of chromatographic analysis parameters [11]:

$$I = 100 \frac{\log t'_{R(x)} - \log t'_{R(n)}}{\log t'_{R(n+1)} - \log t'_{R(n)}} + 100n \, ,$$

where $t'_{R(x)}, t'_{R(n)}, t'_{R(n+1)}$ – the adjusted times of test sorbate retention and n-alkanes with carbon number n and $n+1$, eluting before and after the investigated sorbate.

The values of differential molar free adsorption energy of test compounds were calculated using the given formula [9]:

$$\Delta G_i = -2.3RTb \, ,$$

$$\Delta G_i = -2.3RT \left[\frac{I - 100n}{100} b + \log \frac{V_{gn}T}{273} \right],$$

where R = 8.314 J/mol·K; T – the column`s temperature, K; $I$ – the compound retention index at column`s temperature T; n – the carbon number value of one of the referent n-alkanes; $b = \log t'_{R(n+1)} = \log t'_{R(n)}$; t'_R – the adjusted retention time; V_{gn} – the specific retention volume of n-alkane with a carbon number value equal to n.

The values of specific retention volumes are determined from the formula [11]:

$$V_g' = \frac{3}{2} \frac{(t_R - t_M)F_C \cdot 273.15}{W_S T_C} \cdot \frac{(\rho_i / \rho_0)^2 - 1}{(\rho_i / \rho_0)^3 - 1} \, ,$$

where F_C – the volume velocity of a carrier gas ml/min; W_S – the sorbent`s mass, g; $T_C$ – the column`s temperature, °C; ρ_0 – the barometric pressure, Pa; ρ_i – the pressure in the column inlet, Pa.

Also, the calculation of thermodynamic adsorption`s characteristics is executed on the ground of the specific retention volume. The values of partial molar solution enthalpy are:

$$\Delta H = 2.306R \frac{\log V_{g(1)} - \log V_{g(2)}}{T_1^{-1} - T_2^{-1}},$$

where ΔH – partial molar solution enthalpy, R – universal gas constant; $V_{g(1)}$ and $V_{g(2)}$ – specific retention volumes at a temperature from columns T_1, T_2.

Isosteric heat of adsorption Q:

$$Q = \frac{\ln(V_{g(1)} / T_1) - \ln(V_{g(2)} / T_2)}{T_1^{-1} - T_2^{-1}}.$$

As noted previously, all calculated parameters are archived and used in further analyses.

3. Automation of chromatographic data processing

From an organizational point of view, the simplest but the least efficient approach of the operations mentioned above is the hand calculation with a help of a scientific calculator. The drawbacks of this approach are clear. Firstly, the analysis of large data volumes requires considerable time expenditures. Secondly, the error possibility is increasing with the complexity degree of applied mathematical methods of data processing. The detection and elimination of them may require additional efforts [5]. Thirdly, the raw data as well as the results of their analysis are kept without strict binding to a define format. That fact complicates their further appliance and perception by other members of collective. All complications mentioned above take place in the processing of chromatographic parameters. Within these frameworks, it is necessary to automate this process.

3.1. Methods of data processing automation

Despite the fact that the most obvious decision is to use some special software, which is oriented to data processing of physical and chemical investigations, their appliance appears to be still limited. Thus, one can talk about the 'flexibility' as one of the key requirements for software solutions. That limits the appliance of the proprietary products with a closed source.

As an example of an alternative decision, the development of special software solution can be considered. This solution can be generated using one of the object-oriented languages of high-level software engineering (such as C#, Visual Pascal, C++ etc.) and meet all requirements to the full extent. However, the imperfection of this approach is the necessity to engage the group of qualified software engineers for the development and maintaining of the software programme. In addition, it requires a particular specialist in the field of system analysis for task formalization and requirement list preparation. It is worth mentioning that as a rule, small research groups do not have enough financial assistance to engage some outside experts.

In view of this fact under the conditions of tight lack of available resources, the software solutions for data processing and storage with increasing frequency are received without engaging of professional software engineers [5]. These solutions are developed on the ground of available office applications and mathematical packages, which are common in the academic environment.

3.2. Methods of data processing automation

Thus, for example, the use of MS Excel spreadsheets is the common decision for chemical data processing [5]. On the one hand, the widespread use of this software solution can be explained with the mass availability of the MS Office package and MS Excel as a part of it. On the other hand, there is a majority of investigators, who are not IT professionals and have enough skills to use a spreadsheet.

The advantages of the MS Excel use are a good structure and visibility of experimental data and results of its processing. Moreover, relatively simple spreadsheets allow performing the organization of big similar data processing in accordance with simple algorithms, which require the sequence of

arithmetical operations and logic condition tests only [5]. Nevertheless, the limitation of the given value set and their target in processing tabular data complicates the realization of more difficult algorithms that can process the results of investigation. Among these algorithms are, for example, value extrapolations of some data array, regression`s modeling, solution of differential equations, Fourier transformations and other algorithmically difficult mathematical methods. To wide extent, the reason of the given drawback is in the impossibility of the direct realization in the field of spreadsheets of cycles and recursions [5]. Despite the fact that the realization of these algorithmic constructions in MS Excel is possible with a help of special software, which is written with the use of Visual Basic for the Applications language (VBA) [5], this process demands the involvement of professionals.

With the point of view of these algorithms realization, the mathematical packages have more potential. Their advantage is their combination of a large set of various mathematical functions with basic programming software, rather simple to be used by someone who is a non-programmer [6]. In general, mathematical packages Mathcad and Matlab are most frequently used for data processing and for scientific work automation, especially in the academic environment. Generally, the given software solutions have similar abilities (in relation to the solution of the generalized problem of processing of data, which were received during chemical experiments). However, they also have their own specificity. Therewith, Mathcad, having a visually oriented input language, is easier in mastering and seems to be a more preferred solution [6]. Besides, the lower academic license cost can also be its merit.

However, with the use of the mathematical package directly for data processing (and for their visualization), it is preferable to save the visibility of numerical data presentation. This is possible due to the appliance of spreadsheets. In this regard, the conceptual model of the solution, which is shown in Figure 1, was accepted.
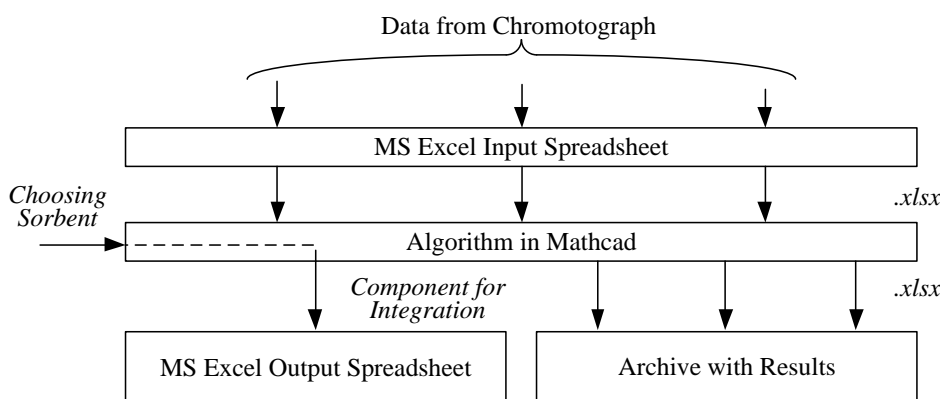

Figure 1. The conceptual diagram of the software solution.

4. Testing of software solution

In accordance with the conceptual diagram in Figure 1, the simple software solution was developed. It solves the problem of chromatographic data storage and efficient processing, as well as it meets all requirements mentioned above.

For the software solution test, the retention times of test compounds and the parameters of chromatographic analyses for the range of sorbents were processed as raw experimental data. Among them were silica gel of Silchrom 80 and the sorbents on its basis, which were adsorptively modified with 8-hydroxyquinoline and 1-phenylazo-2-naphtolate complexes of cuprum (II), cobalt (II) and nickel (II) [9-10]. For the appraisal of chromatographic polarity and selectivity of investigated chromatographic materials, the organic compounds of various classes were used: alkanes, alkenes, alcohols, aldehydes and ketones, nitro and aromatic compounds.

4.1. Input data setting

The retention times of test compounds, which were aggregated in the MS Excel file, are used as an input of the algorithm realized in Mathcad in the form of a two-dimensional array. It was the input data. In this connection, the time retention value, corresponding to the specific test substance, and experiments` conditions (corresponding to the column`s temperature and to the sorbent) were included in the cell. This cell was located at the intersection of the test compound line and the test condition column. A section of the spreadsheet with input data is displayed in Figure 2.

	A	C	D	E
1	Name	C80 4 Ni(SudanI)2	C80 4 Ni(SudanI)2	C80 4 Ni(SudanI)2
2	Date	April 2016	April 2016	April 2016
3	Temperature	150	170	200
11	hexane	0.487	0.378	0.313
12	heptane	0.628	0.482	0.368
13	octane	0.962	0.699	0.468
14	nonane	1.553	0.948	0.603
15	decane			
16	undecane			
21	ch2cl2	0.357	0.348	0.27
22	chcl3	0.453	0.396	0.312
23	ccl4	0.48	0.411	0.32
24	1,2-dichloroethane	0.6	0.488	0.352
25	nitropropane	2.646	1.483	0.784
26	heptene-1	0.747	0.541	0.399
27	benzene	0.599	0.473	0.349
28	toluene	0.966	0.7	0.459

Figure 2. Part of Excel spreadsheet with input data.

Due to the fact that every column of input data, brought to the programme, represents the set of experiential results with various test substances, produced in the conditions of the fixed column`s temperature and with the single sorbent, its processing was fulfilled separately from other data. These results should be recorded separately too.

Thus, for the choice of analysis data, the standard element of control ListBox was realized in the Mathcad with a help of VBScript (Visual Basic Scripting Edition). It allows choosing the only option from the given set, in which the quantity of elements was defined by the number of columns in the input array.

4.2. Presentation of processing results

With foundation of retention time values, which a chosen array contains, the calculations of target values for each of the used test compound were executed. The results of calculations were shown in the MS Excel form with the use of a Mathcad spreadsheet integrated component. The results of experimental data processing are included in table 1.

Thus, using the example of Silochrom C80, which was modified with 1-phenylaso-2-naphtholates of metals, the appraisal of chromatographic polarity with the use of software calculated values ΔG, ΔH, Q was realized. These data are convenient to compare with characteristics of other sorbents in order to choose the best one for separation of a definite class of organic compounds.

Table 1. Fragment of table with calculated chromatographic parameters and thermodynamic data for Silochrom C80 modified with 1-phenylaso-2-naphtholate of nickel (II)

Agents	t_R	t'_R	V'_R	V_g	*I*	ΔG	ΔH	*Q*
Benzene	0.60	0.35	10.47	1.69	675.00	3.31	37.87	4.98
Etanol	1.37	1.12	33.63	5.42	878.00	7.52	98.54	12.27
Butanon-2	3.91	3.66	109.77	17.68	1084.00	12.15	55.76	7.13
Nitropropan	2.65	2.40	71.88	11.58	1010.00	104.65	55.15	7.06
Pyridin	20.05	19.80	594.03	95.70	1378.00	18.89	82.06	10.29

5. Conclusion

With a use of software package Mathcad, combining with the MS Excel spreadsheets` abilities, the method of chromatographic information processing, which allows handling the big data volume, was developed. The big data volumes show the information about the date and the investigation`s objects (analytes` nature and sorbate materials, which were used), physical properties of a chromatographic process (column`s temperature, carrier gas speed, pressure in a column inlet etc.). Besides, they show the direct results of chromatographic analyses (times of analytes retention). The received method allows processing chromatographic data quickly and with satisfactory accuracy, giving the results of retention parameters` calculation and thermodynamic quantities of analytes` sorption in the format, which is convenient for the further interpretation.

Based on the data, obtained from approbation of the introduced solution, it is shown that the modification of Silochrom leads to a decrease of investigated sorbent`s polarities in relation to electron-donating molecules. The ΔG volumes are minimal for aromatic compounds. It is connected with their lower ability to create π-complexes in comparison with other kinds of molecular interactions. Molar adsorption energy of the methylene unit increases in reference to the unmodified silica gel, which is reflected in the increasing of n-alkanes elution time.

The realized software solution allows a chromatographist to make modifications and additions to the data processing algorithm on their own. It widens the limits of its applicability for calculation of various values on the basis of chromatographic retention parameters for the purpose of the detailed survey and the characteristic of new sorption materials.

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