ISBN 963 481 632 0
Acta Phys. et Chem. Szeged 33 131-144 (1987)

THE ZX 81 AS AN INTEGRATOR

By

T. KATONA and I. PÁLINKÓ

Department of Organic Chemistry, József Attila University
Szeged, Hungary

(*Received 6 October 1987*)

The paper summarizes the application of a ZX 81 microcomputer as an integrator. The necessary modifications in the hardware, the principles of the integration and the actual integration software are briefly described. Experience revealed that this computer-integrator is a useful tool in both qualitative and quantitative evaluation of even complicated chromatograms, though it is less accurate than a professional integrator.

Introduction

Gas chromatography permits the analysis of complex mixtures both qualitatively and quantitatively. Qualitative analysis requires a knowledge of the retention times, while for quantification the areas of the peaks are needed. These data are measured by specially built computers, which can even control the gas chromatograph. The modern instruments have built-in computers, while specially built simple computers developed for integration purposes can be attached to the older models.

In the following, a cheap and simple integration method will be presented. An integration program has been written which runs on a simple and cheap home computer (ZX 81).

The computer allows fast data acquisition, a suitable program facilitates the data processing, the results can be stored (and reprocessed with other parameters if necessary), and other programs can be run on the computer as well.

The advantage of writing an individual program is the higher flexibility, and the possibility of fitting it exactly to the problem to be solved. Of course, drawbacks also exist. The main problem is the lack of the sophisticated software which the powerful integrators have; however, these software products are usually well protected by the manufacturer. Therefore, only a few detailed descriptions of such software are to be found in the literature. The manuals of the integrators emphasize the practical aspects; they show how to use the software, but they do not give a description of it [1, 2].

This paper describes the hardware, the elementary steps of the integration procedure, their actual representation on the ZX 81, and finally our experience with the computer-integrator.

Hardware

The CPU (Central Processing Unit) of the ZX 81 is a Z 80A microprocessor. This is used in most of the microcomputers found in Hungary. This model has been developed especially for home computers (HC). It is simple and cheap, though it has all the necessary features. Thus, it can be used as an integrator [3].

The set-up consists of the following parts:

ZX 81 - home computer
16 K RAM - memory extension

SEIKOSHA 50	-	dot matrix printer
JUNOSTY	-	television
MK 29	-	tape recorder

The hardware has been modified somewhat to enhance the reliability of the computer. The original keyboard has been changed to a push-button one, the memory extension has been built into the box of the computer, and a RESET button has been added.

The analog-digital converter (ADC) is a product of INTERSIL. This is a converter with 12 bits, working in the DUAL-SLOPE mode with a 30 ms conversion time. The ADC has been attached to the computer through an 8255 PPI circuit. The ZX 81 has a simple address decoding system, therefore the A5, A6 and A7 address lines and the RD, WR and IORQ lines have proved satisfactory. The output signal goes through an amplifier attached to the RECORDER output of the gas chromatograph [1, 4, 5].

Integration

The integration of the gas chromatographic peaks was earlier performed by two methods. The first was the measurement of the weights of the cut out peaks on an analytical balance, while the second was a simple mathematical operation, i.e. multiplying the peak height by its half-width. The former method can be applied well if the chromatogram consists of asymmetrical peaks; the latter gives satisfactory results if the peaks can be approximated by Gaussian curves. If the above conditions are not met, the determination may contain considerable error [6, 7].

Our integration method resembles the latter procedure, as the computer measures the peak height at given time intervals, performing the integration by the addition of partial peak areas. The data acquisition occurs on-line. There are two processing methods: one is a real-time method, while the other proceeds after the collection of a sufficient number of data (they are stored temporarily by the computer). The accuracy depends on the accuracy of the peak height measurement (i.e. how many meaningful digits are contained by the number formed as the result of the conversion) and on the time interval between samplings (which is determined by the speed of data acquisition).

In our case the AD conversion occurs on 12 bits, which means decomposition of the analog signal to $2^{12}=4096$ parts. The speed of data acquisition is limited by the sum of the conversion time of the ADC and the time required for temporary data storage. Obviously, the frequency of sampling is limited by the capacity of the accessible memory of the computer. This factor is quite significant, because we have only a 16 kbyte RAM.

The reliability of the integration largely depends on the program's being able to distinguish between the baseline and the peaks. For this, we need criteria which allow straightforward evaluation without too many operations.

Baseline corrections

The stability of the baseline is an absolute must during the measurements, but it often changes, and increasing attenuation makes it noisy. There are three methods to record the baseline.

The simplest method is to take its initial values constant throughout the analysis. The disadvantage of this method is that changes in the baseline are not taken into account, and the criterion of reaching the baseline is recovery of the initial value (Figure 1).

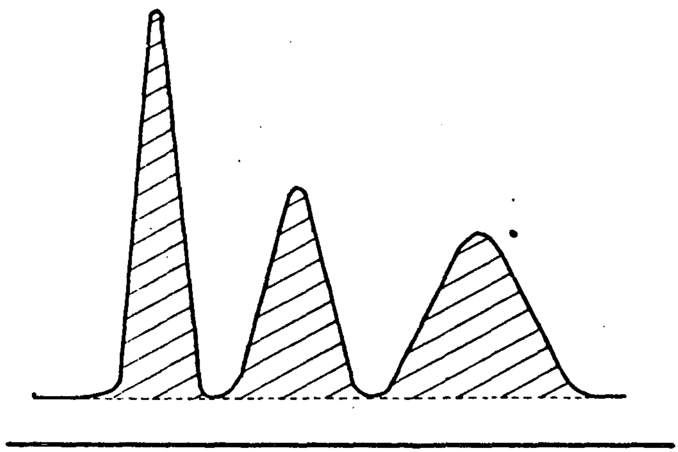

Figure 1.: Integration taking into account the initial value of the baseline.

The second method takes into account the value of the baseline at the end of the chromatogram as well. The change between the initial and the end values is taken as linear and the peak areas are corrected accordingly (Figure 2).

This method can be applied if the baseline is constant, or its tendency to change is constant throughout the analysis.

The third method assigns two baseline values to each peak, one before and another after the peak. Thus, the variation in the baseline can be tracked accurately, and therefore the peak areas can be corrected precisely (Figure 3).

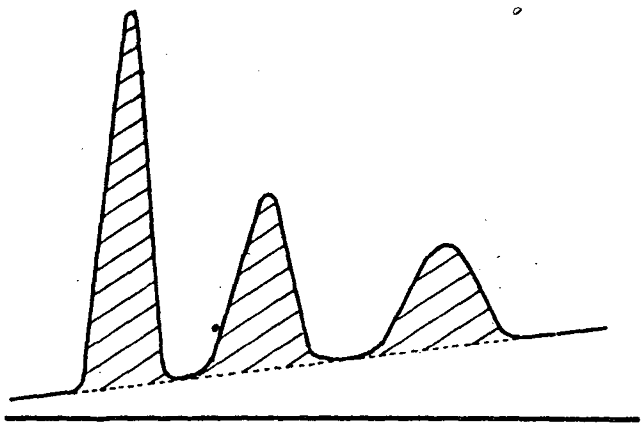

Figure 2.: Integration following the initial change in the baseline.

Peak recording

There are three methods for recording the peaks. They are closely related to the methods of baseline correction.

The first method takes the baseline as constant and records every signal above a given value as a peak. This method can only be used if the resolution is perfect and the baseline is stable (Figure 4).

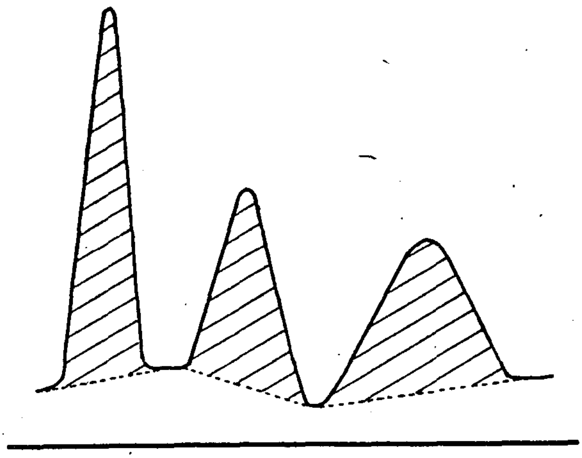

Figure 3.: Integration taking into account the baseline values before and after the peak.

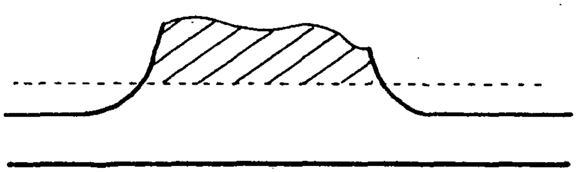

Figure 4.: Peak recording using the constant threshold value.

The second method takes the initial change in the baseline and extrapolates it to the endpoint of the peak (Figure 5).

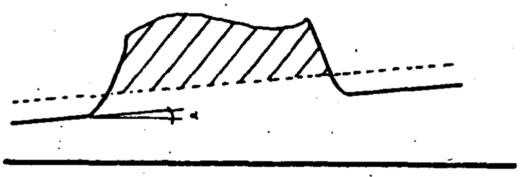

Figure 5.: Peak recording with the extrapolation of the initial value.

The third pays no attention to the baseline, as it monitors the tendency of the variation of the subsequent inputs to vary. A peak is taken as complete when this tendency is below a given value. This method corresponds to the third baseline detecting technique (Figure 6).

The integration software has been compiled in accordance with the third method.

How does the software work?

The integration can be performed in two ways. The first involves parallel data acquisition and data processing, while the second postpones the latter procedure until after the data acquisition. The ZX 81 is quite slow, and so we had to use the second route. The ADC is controlled by an Assembly routine, which runs fast enough to establish 15 inputs/s. The 16 K memory could be filled

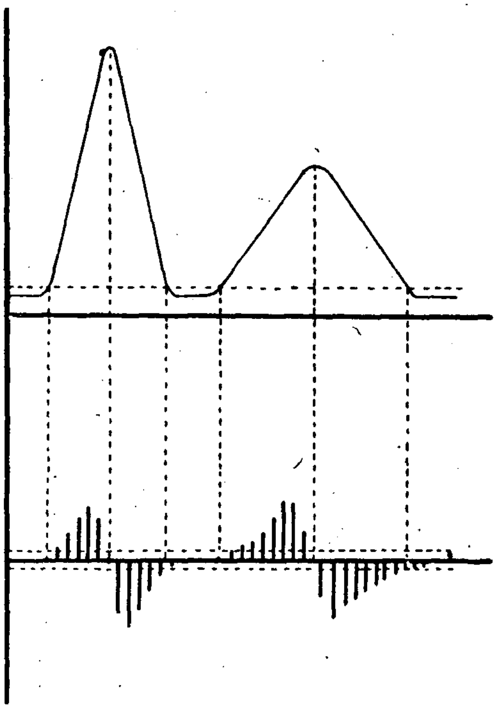

Figure 6.: Peak recording using the changing tendencies.

up quickly in this way, and therefore a cycle in the routine puts the average of more than one inputs into the memory. Accordingly a memory overflow will not occur and the speed of data acquisition can also be varied.

Our experience has shown that the accurate quantitative analysis of a peak with a small retention time requires at least 10 inputs, which means 3 inputs/s if the half-width of the peak is 1.5-2.5 s. If 8 K out of 16 K is reserved for storing the data, then a 12-minute long chromatogram can be recorded. The storage capability has been enhanced by 25 % by shifting and masking the bits not used, thereby saving the valuable digits only.

The control program has been completed with QUICK SAVE and QUICK LOAD routines to save the stored data. We have found that this fast storing capability is suitably reliable. Another addition is the high-resolution graphics, which allows a plot of the chromatogram. This routine requires 8 K RAM, and therefore the input data must be stored on the DISPLAY FILE. This results in a decrease of the resolution to 8 bits and hence this routine can only be used if the accuracy is satisfactory [8, 9].

Another routine sets the FRAMES control register, and its combination with suitable arithmetic and PRINT routines permits the continuous display of the retention time and the input values during the recording of the chromatogram.

The Assembly routines have been compiled into a REM line, and the data processing is done by a BASIC routine [12, 13].

The BASIC routine

The operation of the BASIC routine is based upon the "window" method. A window moves along the chromatogram, so that a relatively small portion of the chromatogram can be examined at a given time. Our program uses three windows: A, B and C. B is the window for the current operations, while A is the previous and C is the next one. Let us see how an integration proceeds.

At the beginning of the peak (Figure 7), the difference between the input sum for C and the sum for B ex-

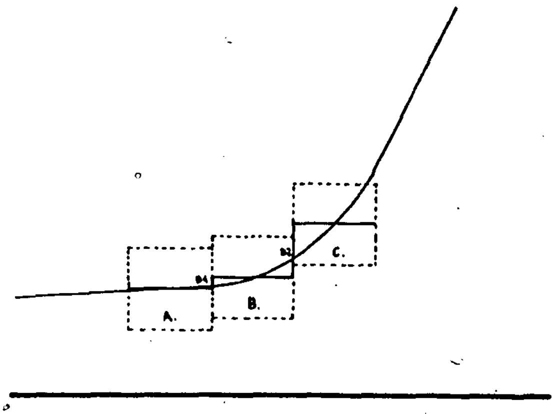

Figure 7.: Integration using the three windows method.

ceeds the threshold value. Window A will give the initial value of the baseline, and B will give the first partial area. At the end of the peak, the difference between C and B decreases to the baseline value, C will give the baseline value and B will give the last partial area. The window method helps the modular programming, and the integration criteria can be reliably programmed as well.

It is also possible to integrate poorly resolved peaks. The software divides them into two parts, with a vertical line at the minimum between the peaks (Figure 8).

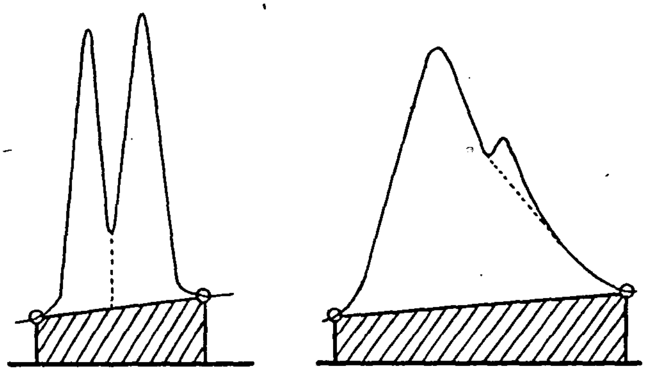

Figure 8.: Integration when resolution is poor

The computer-integrator in practice

The performance of our system had been tested with a mixture of homologous alcohols, the composition of which has been determined with a professional integrator. The variance of the PERKIN ELMER integrator was $\pm$0.5 %, while that of the ZX 81 was at most $\pm$ 2.5 %. The maximum error occurred when the resolution was intentionally worsened.

References

[1] *Chan, C.Z., R. Irwin and R. O'Brien*: International Laboratory 11-12, 54 (1981).
[2] *Hettinger, J.*:-Autolab Technical Bulletin 111, 74.
[3] ZX 81 Users Manual.
[4] ICL 7109 Specifications.
[5] Prof. *G. Buist*, Chemistry Dept., University of Surrey Guilford, Surrey, GU 25 XH, personal communication.
[6] *Stolyarov, B., T.M. Sabinov and A.G. Vitenberg*: Rukovodstvo k prakticheskim rabotam po gazovoi khromatografii., University of Leningrad, Leningrad, 1973.
[7] *Vigdergauz, M.*: Gázkromatográfiai számitások., Müszaki Könyvkiadó, Budapest, 1983.
[8] Mikroszámitógép magazin, Budapest, 4, 23, (1986).
[9] Mikroszámitógép magazin, Budapest, 4, 43 (1986).
[10] *Bóc, I.*: ZX 81 BASIC és ASSEMBLER., Müszaki Könyvkiadó, Budapest, 1985.
[11] *Rákosi, M.*: ASSEMBLER., Müszaki Könyvkiadó, Budapest, 1977.
[12] *Sztrókay, K.*: A Z 80 ASSEMBLER., Müszaki Könyvkiadó, Budapest, 1985.
[13] *Alcock, D.*: Ismerd meg a BASIC nyelvet., Müszaki Könyvkiadó, Budapest, 1983.

ИСПОЛЬЗОВАНИЕ ВЫЧИСЛИТЕЛЬНОЙ МАШИНЫ X 81 В КАЧЕСТВЕ ИНТЕГРАТОРА.

Г. Катона, И. Палинко

В статье обобщены результаты использования микровычислительной машины X 81 в качестве интегратора. Кратко описаны необходимые модификации хардвера, общие принципы и программа актуальной интеграции. Экспериментально подтверждено, что предлагаемый вычислитель-интегратор пригоден для качественной и количественной оценки даже сложных хроматограмм, несмотря на то, что точность его уступает специальным интеграторам.