

## **AUTOMATIC PROCESSING OF MASS SPECTROMETRIC AND CHROMATOGRAPHIC DATA TO OBTAIN STRUCTURAL INFORMATIONS**

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### **Abstract**

The paper describes the realisation of a software application dedicated to the processing of data supplied by a mass spectrometer. Raw data are acquired while performing experimental studies of organic molecules structure.

The software allows the efficient usage of chromatographic and mass spectrometric data in GC-MS experiments and the exhibition of the results in an easy to use and handle manner.

The paper shows examples of structural determination of some compounds from complex mixtures. Structural, as well as quantitative data, obtained in the case of a GC - MS coupling, are presented.

**Key words:** Data processing, mass spectrometry, chromatography, organic compounds.

### **1. INTRODUCTION**

Mass spectrometry is an analytical technique of high complexity[1-2], capable to supply a large quantity of structural data, in the field of molecular research[3-6]. Data are acquired via an acquisition board running with an acquisition rate of 7 k. samples/second. The intensity of the ionic signal supplied by the electrometer as well as the signal supplied by the massmeter are read and stored in a data file. In this file, records consisting of: the spectrum name, the acquisition time - the moment when the scanning starts - the spectrum size - the number of the peaks -, and a vector of maximum 500 elements staying each of a field containing the ion mass and a field containing the peak height, are written. A sequence of such records realises a chromatogram and incorporates at the same time all the information concerning the mass spectra[1-2].

The processing of data contained in this file has to allow a graphical presentation of the signal supplied by the gas chromatograph versus time, namely the total ion current versus time (the chromatogram) and the variation of the signal corresponding to a chosen mass versus time (a fragmentogram)[1]. At the same time, in order to identify the compounds separated by the gas chromatograph, the mass spectra have to be

presented, for the comparison with spectra shown in catalogues or for comparison among them when the chromatographic separation isn't perfect. For reports purposes the printing of chromatograms and mass spectra is necessary[2].

## 2. PROCEDURE DESCRIPTION

A software application was elaborated in order to fulfil the requirements listed above. The program is structured on several modules each of which treating a specific task.

The procedure *GCromaInit* takes from a file the initial starting data and initiates the variables. The user, via a graphic interface, may modify the data read from the “init” file.

The procedure *LoadCalib* loads in a pointer list a table, which serves to adjust, by interpolation, the mass signal, supplied by the massmeter.

The procedure *LoadData* loads in a pointer list the records from the acquired data file. The use of these pointer lists leads to an economic memory management and operation rapidity.

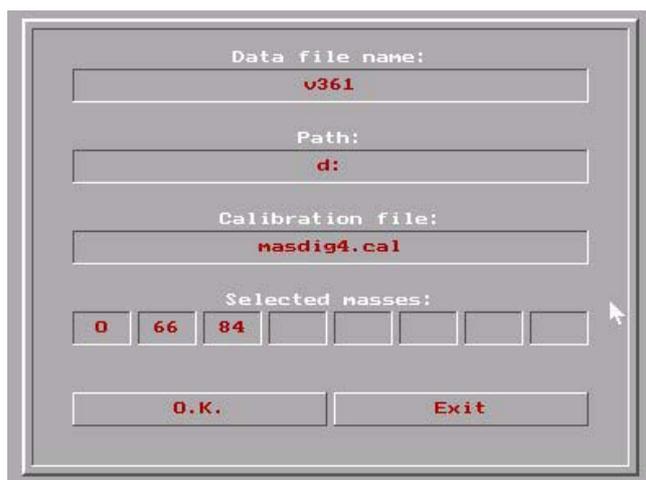
The procedure *Proceed* achieves the effective data processing. It calls the procedure *DrawCroma* that builds the chromatogram and the fragmentograms. *DrawCroma* calls the procedure *DrawSpec* that exhibits the mass spectra.

The procedure *GCromaDone* releases the allocated memory and rewrites the init file putting in it the last used values.

The Procedure *HardCopy* offers the possibility of printing of chromatograms and mass spectra.

The hardware requirements are minimal. An AT386 PC running under MS-DOS 6.2 suffices.

A graphic interface allows the interaction user – program. The user has at his disposal buttons, which can be actuated by the mouse. When the program is launched, the *GCromaInit* procedure displays the dialog window shown in **Fig.1**.



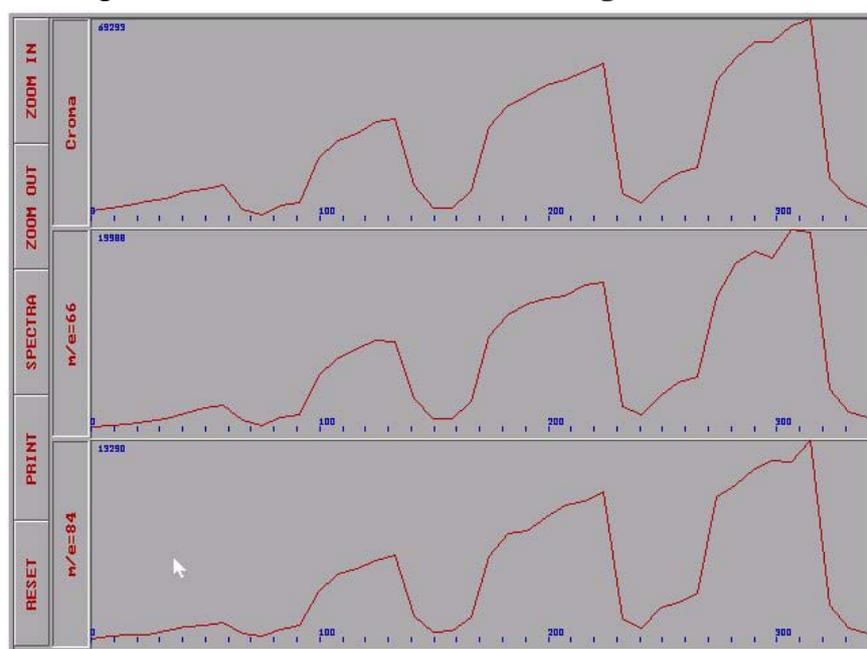
**Figure 1.** The Dialog window *GCromaInit*

The first field contains the data file name, the second field shows the path to this file, and the third field contains the calibration file name. In the next register the user may select up to 8 values representing the mass numbers for which the fragmentogram will be drawn. Zero means the chromatogram. To modify the content of any field in this window, one makes inside a click with the left button of the mouse. The written value disappears, the field becomes shiny and the new value may be introduced from the keyboard. The

new value is validated by pressing <ENTER> or <TAB>. Pressing the “Exit” button, the procedure “*GCromaDone*” is called. The allocated memory is released and the control is passed to the operating system. Pressing the “OK” button calls the procedures “*LoadCalib*” and “*LoadData*”, and then the control is passed to the “*Proceed*”

procedure. The chromatogram (fragmentograms) corresponding to the specified masses are drawn (**Fig. 2**). The display is divided in a number of windows equal to the number of selected masses. In Each window a scale divided in tens of seconds is placed. In the left side of the display there are five buttons with the following functions:

- ZOOMIN enlarges, by representing on the whole screen, an area left – right side delimited with the left mouse button;
- ZOOMOUT returns the original drawing;
- SPECTRA allows the drawing of mass spectra. This subject will be developed later;
- PRINT realises hard copies of the display shown in **Fig. 2**;
- RESET brings back the initial window shown in **Fig.1**.

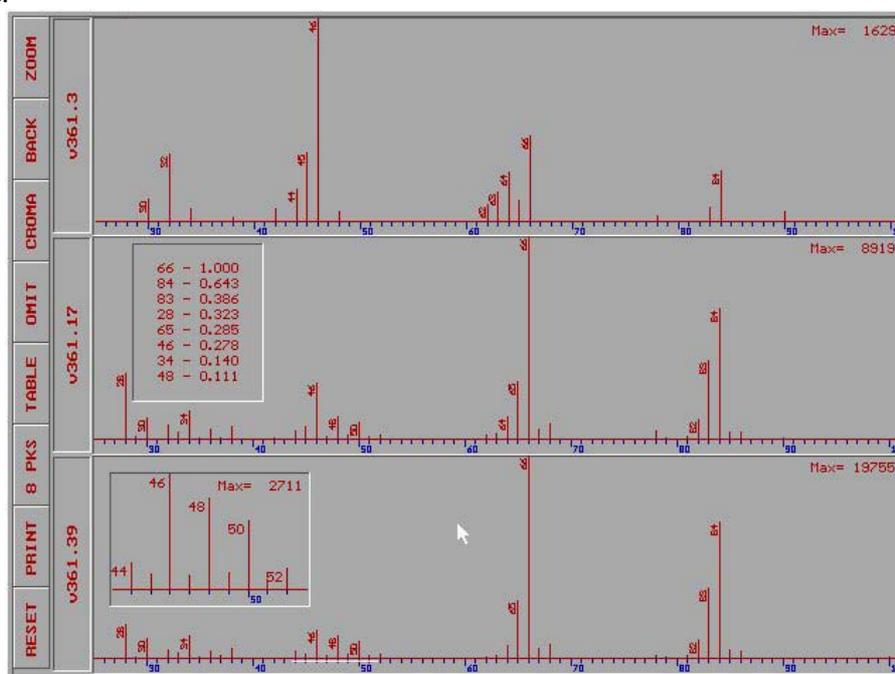


**Figure 2.** Cromatogram and fragmentograms drawn by the “*DrawCroma*” procedure

To represent the mass spectra one have to left click on the button “SPECTRA”. Then one have to select with the left mouse button the position (or the positions) of the spectrum (or spectra) wishing to be displayed. It is possible to select up to 8 spectra. When clicking with the right mouse button, the display is divided in a number of windows equal to the number of the positions selected, and the mass spectra are displayed. In the left side of the display there are 8 buttons with the following functions:

- ZOOM allows the enlarged representation of a domain from the mass spectrum, selected with the mouse. This representation is shown in a window with the position and size chosen by the user acting with the mouse on graphic surface;
- BACK brings back the original image;
- CROMA brings the chromatogram on the screen permitting the selection of other mass spectra;
- OMIT allows the omission of the peaks selected with the left mouse button, when drawing the mass spectrum. The right mouse button starts the redrawing;
- TABLE displays the mass spectrum, normalised to the unity, in a table form.
- 8 PKS lists, in a window, the first 8 peaks in decreasing intensity order. This information is very useful when consulting the mass spectra data bases;

- PRINT allows printing of hard copies from the display image;
  - RESET brings back the dialog window drawn by the *GCromaInit* Procedure.
- The function "TABLE" as well as the function "8 PKS" may be launched also after the action of the "OMIT" button. Each time, the "BACK" button brings back on the display the initial spectrum in graphic form. **Fig. 3** shows the screen displaying mass spectra.



**Figure 3.** Mass spectra drawn by the procedure DrawSpec. In the v361.3 spectrum the peak with the mass 28 was omitted. In the v361.17 spectrum the most intense 8 peaks were listed. In the v361.39 the mass domain 44 – 52 was shown under zoom.

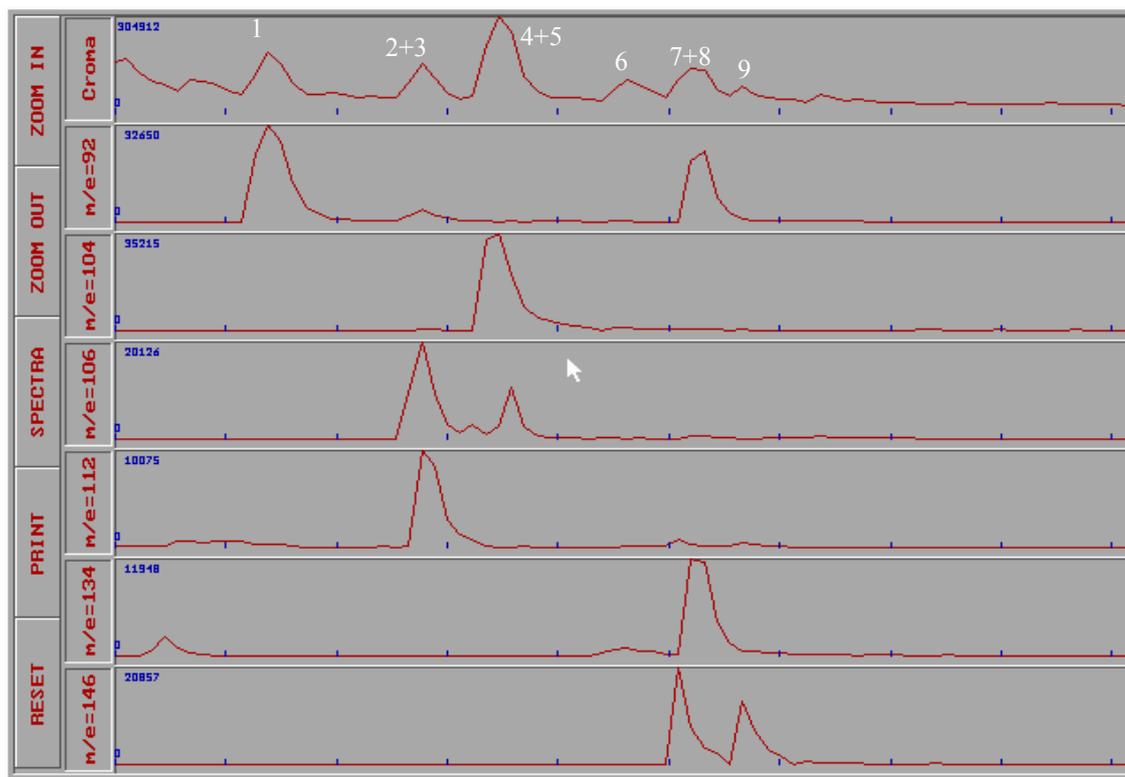
### 3. APPLICATIONS. DETERMINATION OF MOLECULAR STRUCTURE

To determine molecular structures, the following type of information are necessary[3,4]:

- Data about the quantity of substances;
- Data about the nature of the matrices and the possibility to eliminate the interference;
- Elements for deducing the elemental formulae, functional groups and spatial configuration.

It is possible to use, at the same time, the chromatographic and the mass spectrometric data. The software contains the specific modules for the selection of the data in every step, namely:

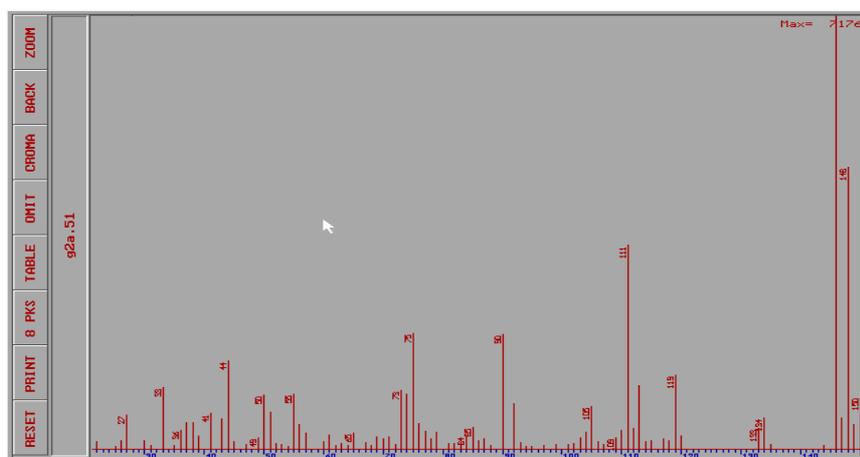
1) To calculate the relative concentration of the compounds, the area under the curve corresponding to the total ion current is used. In the situation when an interference of two or more compounds (chromatographic coelution) appears, the compound quantity is deduced by using selected ions[1,5,6]. In **Fig. 4** the separation of some organic compounds (aromatic compounds) from an environmental sample is shown. The peak 2 consists of three compounds: p-Xylene, m-Xylene and Chlorbenzene. To obtain the compound concentrations, the ions  $m/z$  106(m-Xylene+p-Xylene) and  $m/z$  112(Chlorbenzene) were used.



**Figure 4.** The GC/MS separation of the compounds from an environmental sample

Two compounds coexist, also, under the peak 5,; n-Butylbenzene and Dichlorbenzene probable 1,3. These compounds form a broad peak in the total ion chromatogram, but two distinctive peaks using the selected ions m/z 134 and m/z 146 respectively (see **Fig.4**).

2) The determination of the chemical structure is based on mass spectrum configuration of every compound[4-6]. Mass spectrum contains basically two type of information: ionic abundance and mass of the ion (m/z). Analysing the intensity distribution and the corresponding m/z ratio, the structure of every compound can be deduced.



**Figure 5.** Mass spectrum of the compound 7 from an environmental sample (identified as orto-dichlorobenzene)

In **Fig. 5** the mass spectrum of 1,2(orto) Dichlorbenzene is shown. The main ions are: M=146, the molecular ion (base peak), and m/z 111 obtained by the loss of one

Cl atom. Both ions have a very characteristic structure due to the isotopic distribution of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  (naturally 3:1 approximately). The peaks  $m/z$  111 and 113 are in the ratio of 3:1 (this fragment ion contains only one Cl atom) but the ions  $m/z$  146, 148 and 150 are in the ratio of 9:6:1 (molecular ion contains two Cl atoms).

The compounds relative concentration and identity are shown in Table 1.

**Table 1.** The relative concentration (%) and identity of compounds from an environmental sample

Nr. Peak	Concentration (%)	Identification
1.	22.30	M=92: Toluene
2.	15.38	M=106: (m+p) Xylene
3.	7.69	M=112: Chlorbenzene
4.	13.46	M=104: Styrene
5.	8.07	M=106: o-Xylene
6.	0.77	M=134: i-Butylbenzene
7.	16.15	M=146: (m+p) Dichlorbenzene
8.	8.46	M=134: n-Butylbenzene
9.	7.69	M=146: o- Dichlorbenzene

### 3. CONCLUSIONS

The experimental data resulting from combined gas chromatography – mass spectrometry studies can be easily processed in order to find out the chemical structure and relative concentration of organic compounds.

The presented software can supply important information concerning the studied compounds separated from the matrices interference (interference elimination)

The software presents a friendly graphic interface, enabling a very easy use and the results may be reported in different formats.

### 5. REFERENCES

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