Introduction

Mass spectrometry (MS) is an instrumental technique which enables identification of unknown substance or determination its structure from mass spectrum. Identification of any chemical compound, for which mass spectrum can be found in popular data bases (e.g. NIST [1] or Wiley [2]), is an easy and routine task. It is usually realized by means of library search techniques [3, 4] depending on computer-aided comparison of investigated spectrum with those gathered in available MS data bases. When spectrum of unknown was not included into available collections of reference spectra its analysis can be performed by means of chemometric methods applying either isotopic profiles [5, 6] (in case of organometallics) or spectral classifiers [7, 8] (in case of typical organic compounds, i.e., containing C, H, O, N atoms in molecules). The latter represents mathematical algorithms based on multivariate methods, such as principal component analysis (PCA) [9, 10]. The primary goal of spectra classification is to find correlation between the properties of chemical compounds and their mass spectra. The results of classification reflect structural features that are determined by fragmentation ions appearing in a mass spectrum as characteristic bands.

The main idea of PCA is to reduce the dimensionality of a data set in which there are a large number of interrelated variables, while preserving as much as possible of the variance present in the data set. In relation to mass spectrometry, the data set consists of mass spectra of different compounds in which the intensities of individual m/z ratios are the original variables. PCA also serves as a very good visualization tool, which causes the relationship and clusters become more apparent.

Regarding to the classification of mass spectra, up to now PCA has been used exclusively for typical organic compounds but never for organometallics. It is well known that spectra of the latter substances in contrast to those of the former contain a numerous signals originating from rich isotopic profiles of metals. An exception from this rule is isotopic profile of iron, which indicates a striking similarity to that of carbon. In mass spectra of both elements there is a predominant signal of the main isotope ($^{56}$Fe or $^{12}$C, respectively) exhibiting intensity over 90%. In view of all above facts the authors of present work decided to check, whether classification methods elaborated and used for low-resolution mass spectra of typical organic compounds can also be effective for such spectra of organometallics. For this purpose a set

Fig. 1. Structural formulas, NIST [1] numbers (#) and serial numbers of iron organic derivatives mass spectra analyzed in this work
of mass spectra representing iron organic (carbonyl and non-carbonyl) derivatives and two computer programs MassFeatGen [13] and R [14] being chemometric tools for classification analysis were used.

Mass spectra and methods
For present study 33 low-resolution (obtained by Electron Impact) spectra of iron organic derivatives were taken from NIST 2008 database [1]. 17 of them containing at least 4 carbonyls in molecule were treated as the research set, while the rest 16 characterizing by lack of such substituent were served as the reference set. Figure I summarizes their serial numbers, structural formulas and numbers from NIST database.

At the beginning of chemometric analysis all selected spectra were written to the text files, which contained spectral data (m/z positions of signals and their intensities) as well as basic data identifying each spectrum, such as name of the compound, its mass, summary formula, etc. From them a one file compatible with JCAMP-DX format [15] had been created, which was next introduced to MassFeatGen program [13]. Among many spectral features included in this program two of them, namely: modulo (MD) and autocorrelation (AC), were chosen by the authors for present study. In parameters of both features necessary modifications were done, since their values had been set originally for spectra of typical organic compounds. For studying of iron organometallics spectra the value of difference between two m/z signals in spectrum was changed from 14 (referring to loss of CH₂ fragment) to 28 (expressing loss of one CO). It had been assumed that such modification made possible a detection of carbonyl group in the vicinity (26 and 27) as well as in certain distance to each other (29 and 30). That spectrum the value of difference between two m/z signals in spectrum was changed from 14 (referring to loss of CH₂ fragment) to 28 (expressing loss of one CO). It had been assumed that such modification made possible a detection of carbonyl group in the vicinity (26 and 27) as well as in certain distance to each other (29 and 30). The latter observation is a consequence of significant differences in ionization chamber of mass spectrometer, this molecule formed such process starts with electron knock-out from the free electron pair located on nitrogen atom of its molecular ion and leads finally to the formation of C₅H₁₀N⁺ ion stabilized by resonance (Fig. 3).

It is worth to notice that for present studies also the replicas of the spectra for the same compound recorded by various investigators (e.g., 29 and 27) and those recorded by the same author (e.g., 29, 30 and 31) were considered. The visual evaluation of the data in Figure 2 indicates that the positions representing those spectra are located both in close vicinity (26 and 27) as well as in certain distance to each other (29 and 30). The latter observation is a consequence of significant differences between the intensities of the corresponding m/z signals of various mass spectra of the same compound. Such differences do not disturb classification done in this work, however they inform that correctness of the spectrum of the iron organic derivative 30 should be verified. For such purpose the methods of mass spectra analysis applying isotopic profiles [5, 6] could be very suitable.

Results and discussion
Figure 2 presents the results of PCA into the spaces PC₁ versus PC₂, obtained for 33 mass spectra of iron organic derivatives. Their division on carbonyl containing compounds and those without carbonyls is manifested by the solid line separating respective areas I and II in the plot. One can notice that spectrum of the non-carbonyl compound with serial number 25 is the only one exception from this rule, because of its location in the inappropriate class I.

Such behavior can be explained basing on chemical properties of its molecule C₅H₁₀N⁺Cl⁺FeN⁺. As a consequence of phenomena occurring in ionization chamber of mass spectrometer, this molecule formed C₅H₆N⁺ fragmentation ion having mass 84, which is the multiple of the value 28 corresponding to the mass of CO. High intensity of m/z=84 is responsible for its erroneous inclusion to the class I. According to Biemann nomenclature described in work of McLafferty and Tureček [16], this ion originating during fragmentation represents in mass spectrometry so called cleavage of B type. In case of the compound 25, such process starts with electron knock-out from the free electron pair located on nitrogen atom of its molecular ion and leads finally to the formation of C₅H₁₀N⁺ ion stabilized by resonance (Fig. 3).

Conclusions
The classification performed in this work by chemometric methods routinely used for mass spectra of typical organic compounds enabled division of all investigation spectra of iron organic derivatives on two classes representing: carbonyl compounds containing at least 4 CO groups (I⁺) and non-carbonyl compounds (II⁺). Therefore it can be concluded that the correlation between the compound structure and its mass spectrum was found for iron organometallics. It was also shown that spectrum quality can have the influence on the correctness of spectra classification performed by means of chemometric multivariate methods.

Acknowledgements
The authors thank professor Kurt Varmuza of Vienna University of Technology for providing the MassFeatGen program.

Literature
Irena SZYMURA, Ph.D., is a graduate of the University of Nicolaus Copernicus in Toruń, Faculty of Mathematic-Physics-Chemistry (1974). She acquired her Ph.D. degree in 1982 at the University of Technology and Agriculture (at present University of Technology and Life Sciences) in Bydgoszcz. Currently she is an assistant professor of Department of Chemistry at the University of Warmia and Mazury in Olsztyn. Scientific interests: analytics in environmental protection, physical chemistry of soil.