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Mass Spectrometry - The Important Characterisation Method of Fullerenes

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Abstract:
A sector field mass spectrometer was applied to generate fullerene ions with different ionisation methods. Electron impact ionisation (EI), chemical ionisation (CI), fast atom bombardment ionisation (FAB) and field desorption/field ionisation (FD/FI) were used for the generation of ions. The yield of ions, the molecule fragmentation, multiple ionisation and the detection efficiency of higher and endohedral fullerenes are compared. It was found that the negative ion CI is the best ionisation method for fullerenes. Examples of metallofullerene mass spectra are shown and problems during the recording are discussed.

1 INTRODUCTION

Mass spectrometry is one of the important characterisation methods of fullerenes. Already during the discovery of the new class of carbon structures the hypothesis by Kroto and Smalley [1] based on mass spectrometric investigations.

In the groups of Kaldor [2] and Smalley [1] first examinations of fullerenes were done by direct coupling of the production by laser ablation of graphite in an inert atmosphere with the analysis of the products by a time of flight mass spectrometer. The spectra show a remarkable stability of C_{60} and C_{70} cluster ions relative to the other and only even-numbered cluster ions were observed for $C_{n>40}$, but the low quantities of the fullerenes in gas-phase complicated or even prevented the characterisation of fullerenes by other methods for several years.

The breaktrough in fullerene production and with it in fullerene research was done by Krätschmer and Huffman in 1990 [3]. Graphite rods were resistively heated in a light arc in presence of inert gas (helium) and after toluene extraction of the soot at the first time a bulk of fullerenes was available.

Although since that time other characterisation methods were used, mass spectrometry with its sensitivity and versatility continues to play a crucial role in purity analysis and in discovery of new species of metallofullerenes or derivatives. Whetten and co-workers [4] used laser desorption (LD), electron impact ionisation (EI) and fast atom bombardment (FAB) mass spectrometry. Cox et al. [5] and McElvany et al. [6] studied fullerenes by positive and negative ion chemical ionisation (PCI, NCI). McElvany and co-workers [7-9] published two summaries of the mass spectrometry of fullerenes and describe mass spectrometry of metallofullerenes.

In this paper we report on the influence of the ionisation method of the fullerene mass spectra. Mass spectra of ions generated by EI, CI, FD and FAB are compared to get information about the differences between the measured and the real sample composition, of

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the sensitivity, multiple ionisation and fragmentation of fullerenes. These spectra are complemented through spectra of metallofullerenes produced by our group.

2 EXPERIMENTAL SECTION

Mass spectra were acquired on a sector field mass spectrometer MAT 95 (Finnigan). The spectrometer is suitable for four kinds of ionisation methods (EI, CI, FAB (liquid SIMS), FD/FI) and the detection of generated positive or negative ions. In the case of EI and CI the dissolved samples were applied to a wire loop, dried on air and after insertion into the instrument heated up to 1500°C. The volatile molecules were ionised by an electron beam of different intensity (EI $\Rightarrow$ 70 eV or 15 eV, 1 mA and CI $\Rightarrow$ 150 eV, 100 µA). Methane was used as ionisation gas in CI. The samples studied by FD were dropped onto the FD whisker and ionised by an electric field of 6 kV. In contrast to these ionisation methods the FAB samples were mixed with 3-nitrobenzyl alcohol (m-NBA) and ionised with a cesium ion beam (10 kV). The positive and the negative ions were measured by CI and FAB, but only the positive ions by EI and FD. For each sample the average of all spectra during the evaporation of the sample was taken. The result is a time integral spectrum.

The fullerenes were synthesised by the Krätzschmer-Huffman carbon arc process described above. The apparatus for fullerene production was developed by our group and published in [10]. The helium pressure was 100 Torr and a current of 175 A was used. In case of the metallofullerenes pure metal or metal oxide powders were mixed with graphite powder and pressed into a concentric hole inside the pure graphite rods handled in a dry box. This rods were burned in a 300 Torr helium atmosphere. As metals holmium, lanthanum, praseodymium, thulium and yttrium were used.

The condensed carbon soots were Soxhlet-extracted by toluene, in case of metallofullerenes by carbon disulfide. The resulting fullerene mixture was dried under vacuum. For separation of C_{60}, C_{70}, higher fullerenes and metallofullerenes a HPLC was used. The extract were separated in a two stage mode, first step by a Polystyrole-gel column, second step by a Buckyclutcher column.

All measurements for investigation of the ionisation techniques were carried out with the same mixture of HPLC pure C_{60} and C_{70} (ratio 1 : 1) dissolved in toluene.

The metallofullerenes were measured in a toluene solution of the crude soot extract.

3 RESULTS AND DISCUSSION

The analysis of the mass depending measurements show that the mass spectra of the same sample differ very strongly. Especially the differences in the C_{60} : C_{70} peaks are considerable. In case of the PEI with 70 eV can be observed high fragmentation and multiple ionisation as well as a ratio of C_{60} : C_{70} of around 100 : 20. By decreasing the electron energy to 15 eV the fragmentation and multiple ionisation disappeares, but the sensitivity diminishes distinctly (see Table 1). Using the FAB with cesium ions the sensitivity of the detection of fullerenes is approximately one thousandth of that of the NCI. The adduct formation with the embedding matrix in the case of FAB as well as additional matrix signals below m/z = 600 may cause wrong interpretation of the fullerene mass spectra. It is found that the NCI is the best ionisation method for fullerenes in comparison to PCI, NEI and positive and negative ion FAB (PFAB, NFAB). The sensitivity of the detection by NCI is about a thousand times better than of all other ionisation methods. So NCI can be used to detect traces of fullerenes (endohedral or higher fullerenes) too. Besides the NCI and PFD spectra reflect the real ratio of C_{60} and C_{70} in the best way (Fig. 1-3).

Table 1
Survey of the fullerene mass spectra

ionisation	amount	ion current	ratio C_{60} : C_{70} (±5)	remarks *
PEI 70 eV	1 µl	$3.41 \cdot 10^5$	100 : 20	f, m
PEI 15 eV	10 µl	$2.35 \cdot 10^3$	100 : 30	
PCI	1 µl	$2.19 \cdot 10^5$	100 : 70	a
NCI	**1 µl**	$\mathbf{1.14 \cdot 10^8}$	**97 : 100**	**a**
PFAB	-	$2.02 \cdot 10^4$	100 : 50	f, a
NFAB	-	$4.78 \cdot 10^4$	100 : 50	f, a
PFD	2 µl	$4.20 \cdot 10^3$	90 : 100	m

* f - fragmentation
m - multiple ionisation
a - adducts

All other ionisation methods give a lower C_{70} content in the mixture. Disadvantage of the NCI is the formation of adducts of fullerenes with the ionisation gas (M+14, M+16, etc.). Therefore the detection of other addition products of fullerenes such as oxygen is difficult. Furthermore high sample introduction rates may lead to saturation effects. In this case mo quantitative measurements are possible.

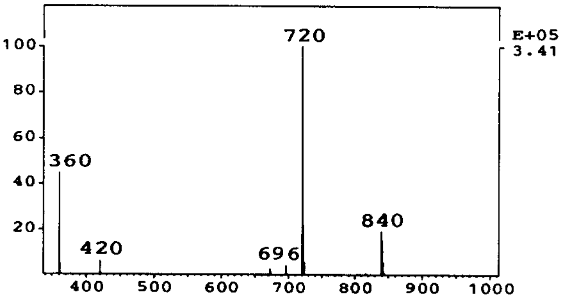

Fig.1: PEI, 70 eV

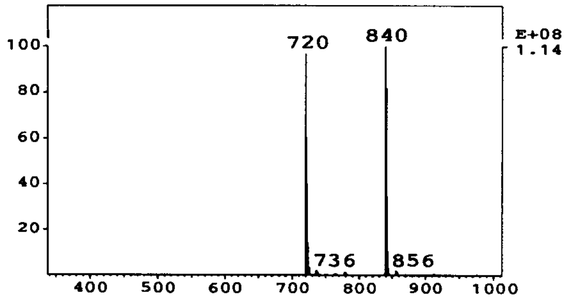

Fig.2: NCI, methane

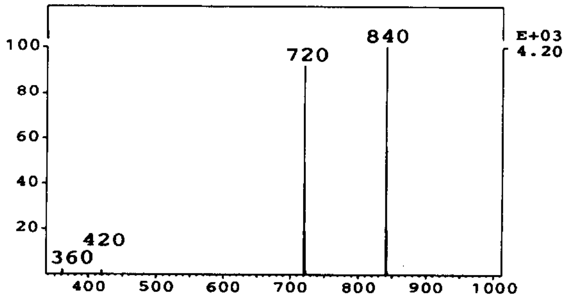

Fig.3: PFD, 6 kV

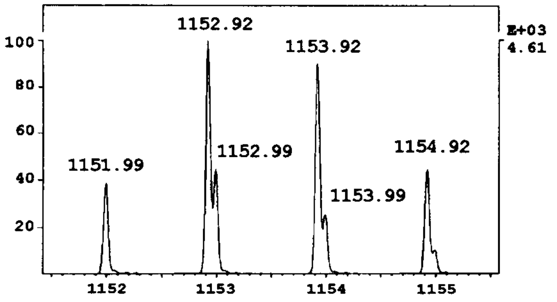

Fig.4: NCI of Tm@C_{82}

In search of new metallofullerenes as well as during the improvement of the yield of metallofullerenes mass spectrometry is playing a key role. Just shortly after a metallofullerene synthesis the result can be examined in the soot extract by mass spectrometry without previous separation. In the samples single and double metallofullerenes are detected (see Table 2). The mass spectra of thuliumfullerenes have to be measured in high resolution mode (m/Δm≥15000) to separate the $^{12}C_{X-1}{}^{13}C$ peak from the $^{169}Tm@^{12}C_{X-14}$ (difference is 0.069 m/z) (Fig. 4).

Table 2
metallofullerenes measured by mass spectrometry

metal	found metallofullerenes
holmium	$Ho@C_{82}$, $Ho_2@C_{82}$, $Ho_2@C_{84}$
lanthanum	$La@C_{82}$, $La_2@C_{80}$
praseodymium	$Pr@C_{82}$
thulium	$Tm@C_{82}$, $Tm@C_{84}$, $Tm@C_{90}$, $Tm@C_{92}$, $Tm@C_{94}$, $Tm@C_{96}$, $Tm_2@C_{80}$, $Tm_2@C_{82}$
yttrium	$Y@C_{82}$, $Y_2@C_{84}$

4 CONCLUSION

Several mass spectrometric ionisation methods are employed to charcterise fullerenes. The comparison of the methods shows that the ionisation by NCI is the best method for the detection of fullerenes in most cases. The advantages of this method are high sensitivity and good recovery of the sample composition. Only for some addition products of fullerenes (for example with oxygen) the CI technique is not suitable.

For performing quantitative measurements of fullerenes by mass spectrometry the determination of the response factors in dependence on the kind of ionisation is necessary. By different techniques of ionisation fragments and adducts of fullerenes can be formed and a misinterpretation of the spectra can occur.

Metallofullerenes can be measured by NCI and have a remarkable stability on air. That could be an evidence for endohedral position of the metal in the fullerene cage.

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