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Production of polyatomic ions by ^{252}Cf-fission fragments and by short laser pulses

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Production of polyatomic ions by ^{252}Cf-fission fragments and by short laser pulses

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PDMS and MALD spectra of oligosaccharides obtained by the same time-of-flight spectrometer from samples, which were prepared by using a technique suitable for both methods, have been measured and compared. By comparing the spectra, the effects of different matrices assisting the production of polyatomic ions have been tested. Matrices enhancing the quasimolecular ion intensity in PDMS, i.e. heteroaromatic amines and phthaleins, turned out to be also suitable MALD matrices if they absorb at the wavelength of the irradiating laser beam.

1. Introduction

Production of polyatomic ions, especially of peptides and proteins, is a routine matter in ^{252}Cf-plasma desorption mass spectrometry (PDMS) [1] and in matrix-assisted laser desorption mass spectrometry (MALD-MS) [2]. Energy deposition in a solid via electronic excitation and transition of surface material into the gas phase followed possibly by fast chemical reactions are fundamental steps in both processes of ion production. The area of desorption is much smaller in heavy ion induced desorption (about 50 nm in diameter) if compared to that of laser induced desorption (about 50 μm in diameter). The average number of secondary ions per incident fission fragment is low (about five) compared to the number of ions per laser pulse (up to a few thousand). In PDMS as well as in MALD-MS, an efficient isolation of the analytes in the sample is required to produce larger ions. For example, adsorption to nitrocellulose has been proven to be very effective for analyzing peptides and proteins by PDMS [3]. But also small volatile molecules like 9-anthroic acid or anthrarobin were successfully used as PDMS adsorption matrices [4]. In MALD, aromatic acids such as 2,5-dihydroxybenzoic acid were commonly used as matrices assisting efficiently the desorption and ionisation of biomolecules [5,6]. The mass range accessible for proteins has been expanded by MALD-MS up to a few 100 000 Da.

PDMS and MALD are also of considerable utility for the analysis of carbohydrates. Recently, underivatized and peracetylated malto-oligosaccharides, ranging in length from four to seven glucose units, have been investigated by PDMS [7]. The results obtained show clearly that underivatized maltooligosaccharides deposited on nitrocellulose yields mass spectra showing only very weak $[M + Na]^+$-ion peaks and indicating poor adsorption to nitrocellulose. But deposition on metallized Mylar foil by electrospray produces mass spectra consisting of dominant $[M + Na]^+$- and of series of weak fragment ion peaks. The extent and type of fragmentation of peracetylated oligosaccharides adsorbed on nitrocellulose can be controlled by the amount of sodium in the sample. The positive ion mass spectrum is dominated by a peak corresponding to the sodium-cationized molecule when a large molar excess of sodium salt is added. But when the sample is completely depleted of sodium, the spectrum shows no quasimolecular ion and is instead totally dominated by fragment ion species. Oligosaccharides having a broad molecular mass distribution, i.e. maltodextrins (α-1,4-linked oligoglucans) and dextrans (α-1,6-linked oligoglucans), have been analysed quite recently by MALD-MS [8]. With both analytes, series of monosodium and monopotassium oligoglucan ions were observed with 2,5 dihydroxybenzoic acid as matrix. The masses of the maltodextrins ranged from 500 to 3500 Da and masses up to 7000 Da were observed with dextrans. It could be shown in one case that the signal pattern of the mass spectrum is comparable to that of a chromatogram using ion chromatography (Dionex) and pulsed amperometric detection.

Recently, we tested and compared systematically a variety of low molecular weight and volatile compounds as matrices in ^{252}Cf-PDMS measurements of oligosaccharides [9]. Some heteroaromatic amines, i.e. 2-aminothiazole, 3-aminopyridine and 3-aminoquino-

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line, hydroxyanthraquinones, i.e. alizarin and quinalizarin, and phthaleins, i.e. fluorescein, respectively, proved to be especially suited to enhance the quasi-molecular ion intensity of oligosaccharides. The suitability of a matrix for oligosaccharide analysis was mainly attributed to the fact that aggregation of oligosaccharides is reduced in the matrix by hydrogen bonding. But the basicity of the matrix compounds may also play an important role, probably in the ionization step.

This contribution focuses on some recent results on oligosaccharides which we obtained by applying both methods, ^{252}Cf-PDMS and MALD. The preparation of samples by a nebulizer specifically developed for producing samples thin enough for PDMS [9] was successfully used also in MALD-MS. The mass spectra were recorded in the same time-of-flight spectrometer. Thus, the results yielded by both methods are not influenced by different sample preparation techniques or different ion optics, and information on the process of polyatomic ion production is obtained directly by comparing the spectra.

2. Experimental

Materials: α-Cyclodextrin was obtained from Prof. P. Köll, Carl von Ossietzky-Universität Oldenburg. The maltooligosaccharides (from maltotriose up to maltoheptaose) were obtained from Boehringer Mannheim GmbH. Dextrin 10 and 3-aminoquinoline were purchased from FLUKA, Buchs, Switzerland, aminopyrazine and 2,5-dihydroxybenzoic acid from Aldrich Chemical Ltd, and fluorescein from Jannsen Chimica. All compounds were used without any further purification.

Sample preparation: The carbohydrates were dissolved in double destillated water at a concentration of 1 mg/ml. The matrices 3-aminoquinoline, aminopyrazine, and fluorescein were dissolved in a 10% (v/v) methanol/water mixture at 10 mg/ml. 2,5-Dihydroxybenzoic acid was dissolved in double destillated water at a concentration of 10 mg/ml. Analyte and matrix solutions were then mixed at a ratio of 1:1 (v/v). For sample preparation, 10 μl of solution were deposited onto an aluminized polyester foil (2.5 μm thick) by the use of a nebulizer. By this procedure, a thin almost homogeneous layer is produced on the foil surface. The nebulizer consists of a glass capillary, a 10 μl microsyringe, and a tube for feeding N_2 as carrier medium.

^{252}Cf-PDMS: The PDMS spectra were obtained with a linear time-of-flight mass spectrometer which was built in cooperation with K. Wien, TH Darmstadt. The spectrometer is equipped with a ^{252}Cf-source (effective fission fragments during the time of this study: about 250/s), 2 MCP-detectors for the start and stop signals, respectively, a 0.8 m drift tube, and with a time digital converter CTN/M2 from IPN, Orsay. The data were collected and stored in an IBM PC/AT computer. Usually, the run time was 30 min, and the acceleration voltage +15 kV. Mass resolution is about 600.

MALD-MS: The MALD-MS spectra were obtained by our linear time-of-flight spectrometer modified for applying laser induced desorption (Fig. 1). The stop MCPs were replaced by a detector unit which is similiar to those applied in other laboratories. It is a venetian blind secondary electron multiplier (EMI 9642 2B) with an additional dynode supplied with a separate negative potential (−3 to −20 kV). A cylindrical tube on ground potential is placed in front of the dynode to shield the drift region from electric fields. The SEM anode is directly coupled to a fast amplifier (input impedance 50 Ω, rise time less than 500 ps) for current to voltage conversion. The focused and attenuated light pulses (15 ns FWHM) of a Q-switched frequency tripled (355 nm) or frequency doubled (532 nm) Nd:YAG laser (Hyperyag from JK) hit the sample in the spectrometer at an angle of 7°. Single shot spectra are recorded by a 125 megasample transient recorder (LeCroy 9400, DSO) controlled by an IBM PC/AT computer. The DSO trigger is generated by a signal of a fast photodiode excited by a laser beam reflex. The photodiode is connected to a constant fraction discriminator for time jitter reduction and for amplitude discrimination. Generally, the spectra presented were accumulated from 20 single shots, but the dextrin 10 spectra were evaluated from 50 shots. A local variation of the laser focus on the sample turned out to be unnessesary due to the sample preparation applied. But a selection of single shots must be made mainly due to the jitter of the laser pulse amplitude.

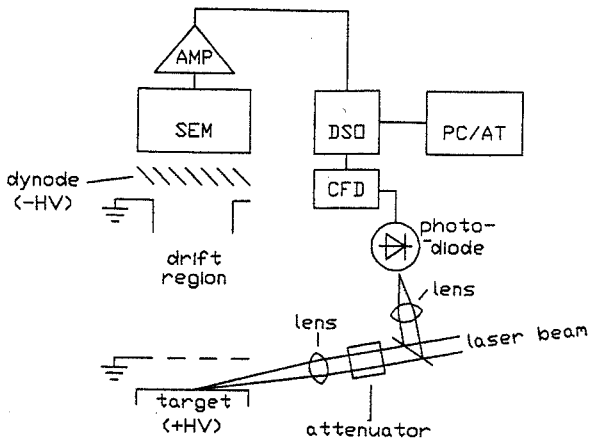

Fig. 1. Experimental setup for MALD-MS.

3. Results and discussion

The compounds chosen as matrices for this study were required to absorb sufficiently the laser beam at 355 or at 532 nm. Additionally, the compounds were chosen for their ability to form hydrogen bonds to the sugar, so that analyte molecules could be isolated from each other. Finally, the compounds were required to be soluble in water or water/methanol mixtures so that they could give homogeneous aqueous or aqueous-methanolic solutions and could be deposited together with the oligosaccharides onto a thin metallized foil by our spraying apparatus. Therefore, we chose the following compounds for comparing PDMS to MALD with regard to matrix effects: 3-Aminoquinoline, aminopyrazine, fluorescein and 2,5-dihydroxybenzoic acid. In a first series of experiments, α-cydodextrin, a cyclic oligosaccharide, was taken as the analyte, but some β-cyclodextrin was also present in the sample due to insufficient purification.

PDMS spectra of α-cyclodextrin obtained with 3-aminoquinoline, aminopyrazine and fluorescein as matrices are depicted in Fig. 2. All spectra show as a general feature dominating peaks at m/z 996 and 1158

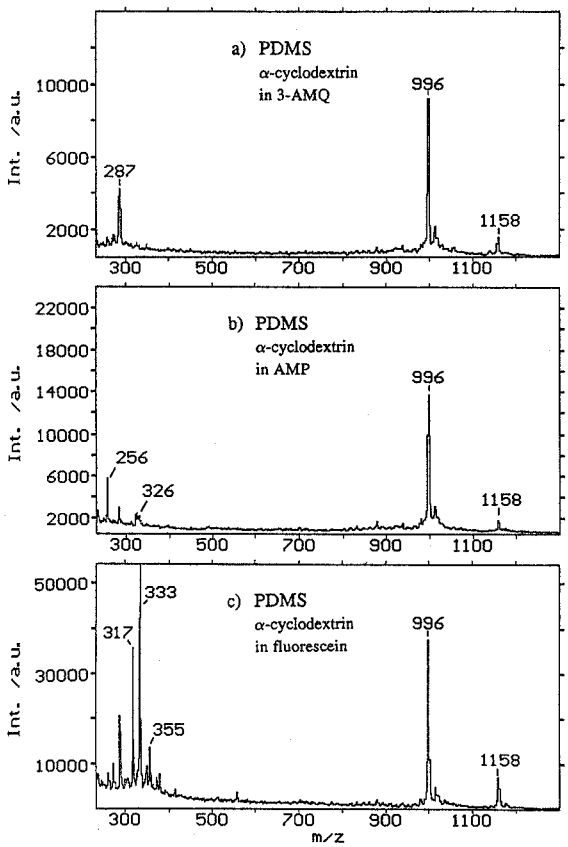

Fig. 2. PDMS spectra of α-cyclodextrin. (a) in 3-aminoquinoline (3-AMQ), (b) in aminopyrazine (AMP), (c) in fluorescein.

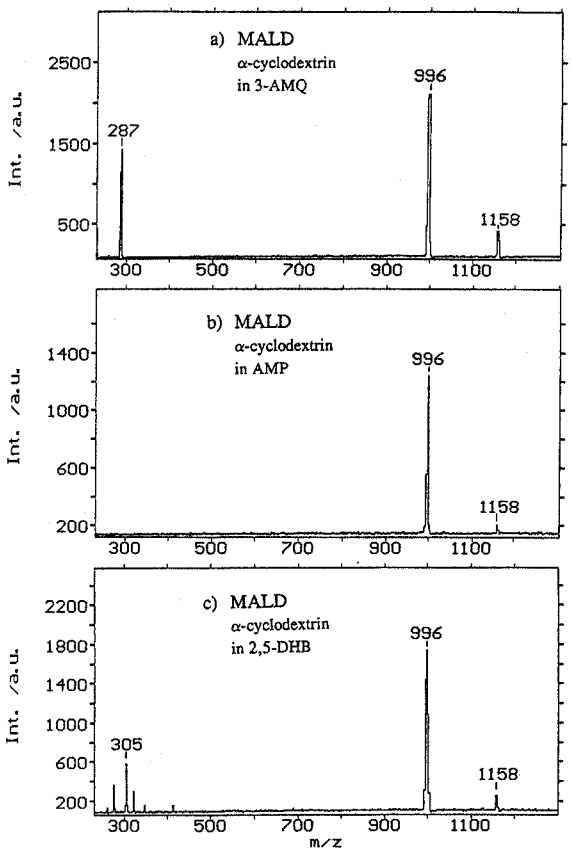

Fig. 3. MALD spectra of α-cydodextrin, irradiation at 355 nm. (a) in 3-aminoquinoline (3-AMQ), (b) in aminopyrazine (AMP), (c) in 2,5-dihydroxybenzoic acid (2,5-DHB).

corresponding to the $[M + Na]^+$ quasimolecular ions of α- and β-cyclodextrin, respectively. In comparison, the fluorescein matrix gives the highest enhancement of the quasimolecular ion intensity, a result which was also obtained with maltoheptaose as analyte [9]. There are also some fragment ions in the spectra, especially at m/z 163 and 326 which correspond to fragment ions consisting of one or two glucose units, respectively. But the intensity of these small fragment ions is clearly decreased by matrix addition indicating a reduction of internal excitations of the quasimolecular ions. The matrix ions were generally observed as $[M + H]^+$.

MALD spectra of α-cyclodextrin obtained at 355 nm irradiation and with 3-aminoquinoline and aminopyrazine as matrices are depicted in Fig. 3. For comparison, a corresponding spectrum obtained by using 2,5-dihydroxybenzoic acid as matrix is also shown in the figure. The suitability of 2,5-dihydroxybenzoic acid as MALD matrix for oligosaccharide analysis has been reported recently [8]. All spectra of Fig. 3 show the quasimolecular ion peaks at m/z 996 and 1158 corresponding to the sodium-cationized cyclodextrins at almost equal intensity. This experimental result clearly

demonstrates that for oligosaccharide analysis not only aromatic acids but also heteroaromatic amines can be used as suitable MALD matrices when they absorb sufficiently at the wavelength of the irradiating laser beam. It also indicates that an efficient isolation of the analytes in the matrix is a crucial common feature of PDMS and MALD matrices.

In PDMS, 2,5-dihydroxybenzoic acid gives almost no enhancement of the quasimolecular ion peak of oligosaccharides [9]. One reason for that may be the fact that the layer produced on the sample foil is less homogeneous and therefore the isolation of the analytes in some places probably less efficient when using 2,5-dihydroxybenzoic acid. If the inhomogeneities have an average size larger than the PDMS but smaller than the MALD desorption area, then the molecular ion yield in PDMS is clearly affected and considerably lower whereas the corresponding MALD yield may be not affected due to the large number of desorbed and ionized molecules. But different significant ionisation processes may also occur.

A MALD spectrum of α-cyclodextrin obtained at 532 nm irradiation and with fluorescein as matrix is depicted in Fig. 4a. Fluorescein has a high absorbance at this wavelength, and the MALD spectrum clearly shows the quasimolecular ion peaks at m/z 996 and 1158 corresponding to the sodium-cationized cyclodextrins. The matrix ions were observed as $[M+H]^+$ at m/z 333, as $[M+Na]^+$ at m/z 355 and some fragment ions at $m/z < 333$. The ion intensities of the cyclodextrins are somewhat lower if compared to MALD spectra obtained with heteroaromatic amines as matrices, but the general suitability of a phthalein as MALD matrix for oligosaccharide analysis is clearly demonstrated. Corresponding experiments with other phthalein matrices, i.e. eosin b and eosin y, yielded comparable results. In the future, one important advantage for using phthaleins as matrices in MALD will be the fact that they absorb at wavelengths being in the visible spectral range.

When using fluorescein as matrix, the sample can be excited also at 355 nm. Thus, the effect of varying the excitation wavelength from the visible to the ultraviolet can be studied, but the irradiance required at

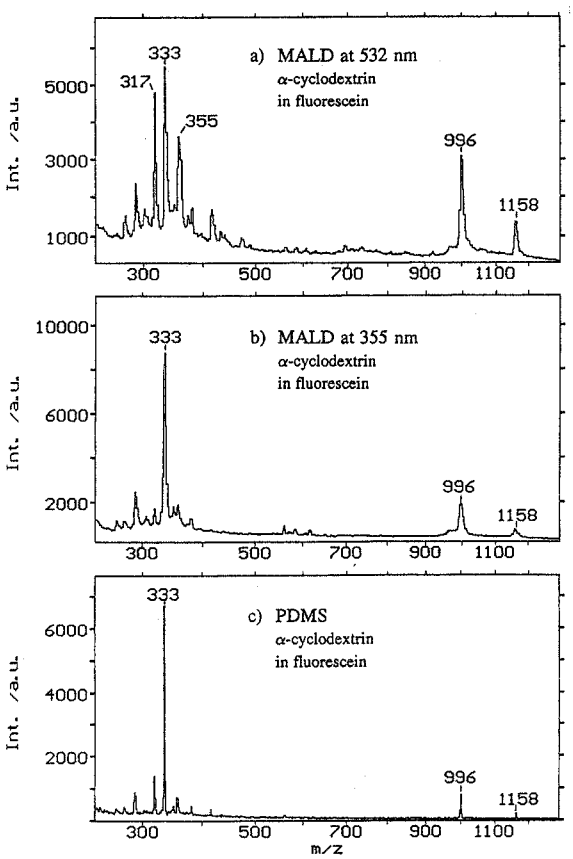

Fig. 4. Mass spectra of α-cyclodextrin, matrix: fluorescein. (a) MALD, irradiation at 532 nm, (b) MALD, irradiation at 355 nm, (c) PDMS.

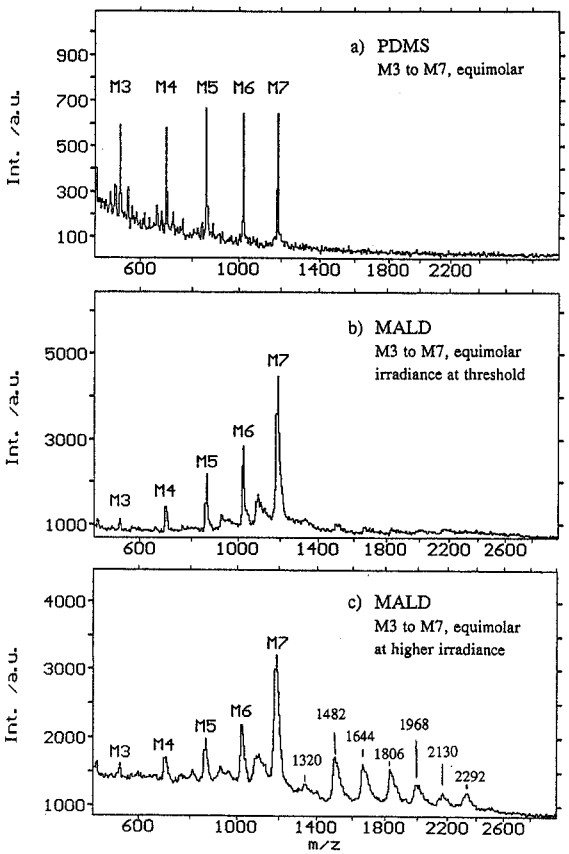

Fig. 5. Mass spectra obtained with an equimolar mixture of maltooligosaccharides, maltotriose (M3) to maltoheptaose (M7), matrix: 3-aminoquinoline (3-AMQ). (a) PDMS, (b) MALD, irradiance at threshold, (c) MALD, at higher irradiance.

355 nm is considerably higher due to low absorbance of the fluorescein matrix. A MALD spectrum obtained from the same sample but irradiated at 355 nm is depicted in Fig. 4b. In comparison to Fig. 4a, the quasimolecular ion peaks at m/z 996 and 1158 do not show significantly less intensities, in spite of the low absorbance of the matrix. The main difference between 532 nm and 355 nm irradiation is rather the ionisation of the matrix molecules. At 355 nm irradiation, nearly all matrix molecules are ionized by protonation, whereas at 532 nm irradiation protonated as well as sodium attached fluorescein molecules were obtained at considerable intensities. Thus, the MALD spectrum obtained at 355 nm irradiation compares much better with the PDMS spectrum than that obtained at 532 nm irradiation. A PDMS spectrum obtained from the same sample is shown in Fig.4c.

In a second series of experiments, we investigated samples prepared with equimolar solutions of five linear oligosaccharides, i.e. from maltotriose (M3) to maltoheptaose (M7), and with dextrin 10, a commercially available α-1,4-linked oligoglucan sample having a broad molecular mass distribution. In Fig. 5, PDMS and MALD spectra obtained with an equimolar mixture sample are presented. The matrix was 3-aminoquinoline and irradiation at 355 nm. In the PDMS spectrum, the quasimolecular ion peaks at m/z 528, 690, 852, 1014, and 1176, corresponding to the sodium-cationized oligomer units from M3 to M7, respectively, have nearly the same intensity. This result reflects the fact that mass discrimination is reduced in PDMS by matrix addition [9]. In contrast, the MALD spectra obtained from the same equimolar mixture sample (see Figs. 5b and 5c) show a drastic mass discrimination in the recorded mass range: The lower the mass, the lower the intensity. Additionally, broad ion peaks at m/z 1320, 1482, 1644, 1806, 1968, 2130 and 2292, respectively, were observed when the irradiance was increased above the threshold (Fig. 5c).

Regarding the mass discrimination observed in MALD, we varied in a series of experiments the matrix (e.g. 2,5-dihydroxybenzoic acid), the sodium content in the sample (by adding up to 5 nMol NaCl), the matrix/analyte molar ratio (from 1:1 to 1000:1), the extrac-

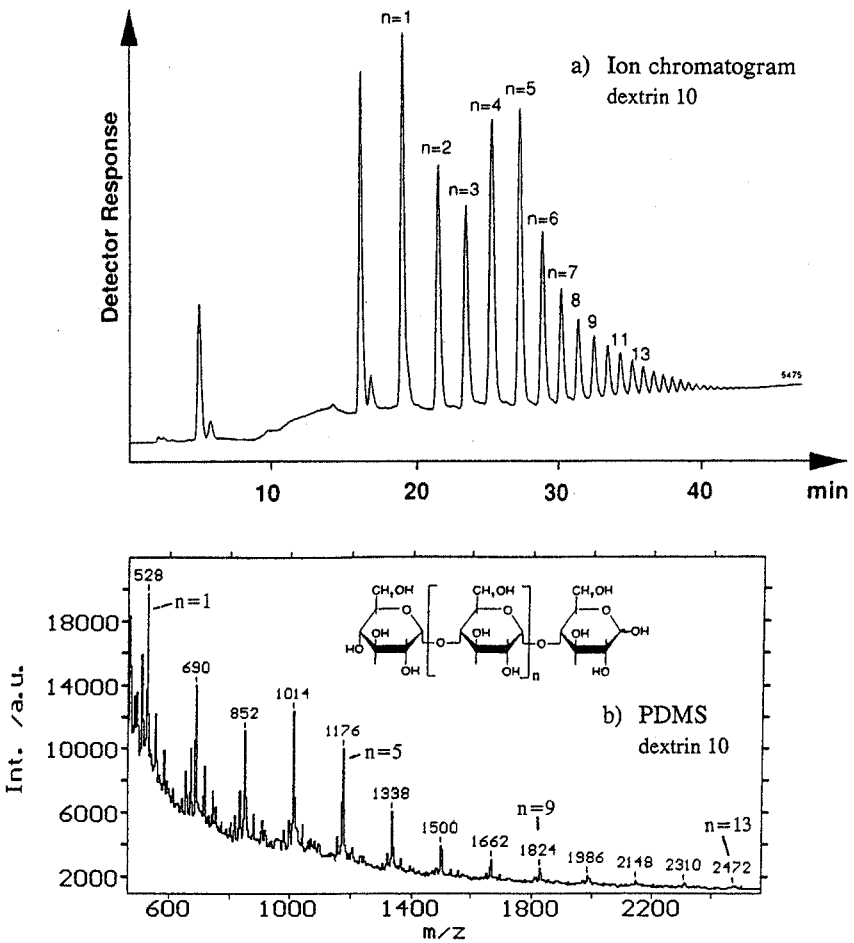

Fig. 6. Dextrin 10. (a) Ion chromatogram (taken from ref. [9]), (b) PDMS, matrix: 2-aminothiazole.

tion voltage, and the laser intensity, but no influence of these parameters on the mass discrimination was observed. We prepared also samples with an equimolar solution of oligopeptides (leucine enkephalin and bradykinin), and in MALD a quite similar mass discrimination was observed, in contrast to PDMS. Thus, we conclude that there are significantly different effects in PDMS and in MALD and we assume that the different sizes of the desorption area affect type and number of secondary ions produced per primary event. For achieving a spectrum in PDMS, the total number of fission fragments is in the range of several 100 000 and each fission fragment produces only a few secondary ions from an area not larger than about 50 nm in diameter. The total number of oligosaccharide quasimolecular ions registrated in a PDMS spectrum is in the range of several 1000. Consequently, these events are rather rare, and mass discrimination does not occur by statistical reasons. In MALD, each single shot produces up to a few 1000 secondary ions from an area which is controlled by the focus of the laser beam, i.e. about 50 μm in diameter, and a few shots are normally sufficient to get a good-quality spectrum. Thus, each single shot contains generally the whole spectrum, and different analytes desorbed and ionized by the same shot compete with each other in the ionisation process. When quasimolecular ions are formed by sodium attachment, discrimination of lower against higher mass ions is probably due to the following facts: (1) Oligosaccharides of larger length have more sites for sodium attachment so that they are favoured by an higher sodium affinity. (2) The formation of quasimolecular ions by sodium attachment is an exothermic reaction. The energy released by this reaction leads to an higher internal excitation in low mass than in high mass ions so that high mass ions survive the ionization more likely.

At higher irradiance, an ion series at higher masses was observed in MALD with 3-aminoquinoline but not with 2,5-dihydroxybenzoic acid as matrix indicating an effect strongly dependent on the matrix (see Fig. 5c). The series starts at m/z 1320 with mass increments of 162 amu corresponding to a single anhydroglucose unit. Therefore, these ions correspond to sugar compounds having higher masses than the analytes. The observed masses indicate that these ions are sodium-cationized anhydro-oligomers, but it is also possible that they are sodium-cationized matrix-analyte compounds. In any case, this experimental result demonstrates that specific reactions occur at higher irradiances when 3-aminoquinoline is used as MALD matrix for oligosaccharide analysis.

A PDMS spectrum and a chromatogram of dextrin 10, which was obtained by using anion exchange chromatography and pulsed amperometry [9], is presented in Fig. 6. In this case, the PDMS matrix was 2-aminothiazole, which has been proven to be an excellent PDMS matrix for oligosaccharide analysis [9]. A series of sodium attached oligoglucan ions is observed in the PDMS spectrum. The molecular weights of the quasimolecular ions range from 528 up to 2472 Da, equivalent to a degree of polymerisation of 3 up to 15. The signal pattern of the PDMS spectrum is closely connected to that of the chromatogram. The chromatogram shows oligomers $n > 15$ at very low concentration, but these oligomers are not observed in the PDMS spectrum due to the background. MALD spectra of dextrin 10 obtained with 3-aminoquinoline and 2,5-dihydroxybenzoic acid as matrices are depicted in Fig. 7. These MALD spectra show also the series of sodium-cationized oligoglucan ions and large oligomer units up to $n = 26$ were observed at intensities which are comparable to the intensities in the chromatogram (Fig. 6b). But in both MALD spectra, the oligomers from $n = 1$ to $n = 5$ are obviously discriminated, in contrast to the PDMS spectrum. Thus, the discrimination in MALD seems to be restricted to ions having masses lower than approximately 1200 amu. But further work and information is absolutely necessary to have an explanation for this experimental fact. Comparing the two MALD spectra, it is concluded that 3-aminoquinoline is in general as suitable as 2,5-dihydroxybenzoic acid for MALD analyses of oligosaccharides. But to reduce aggregate formation, an irradiance near the threshold must be applied when using 3-aminoquinoline.

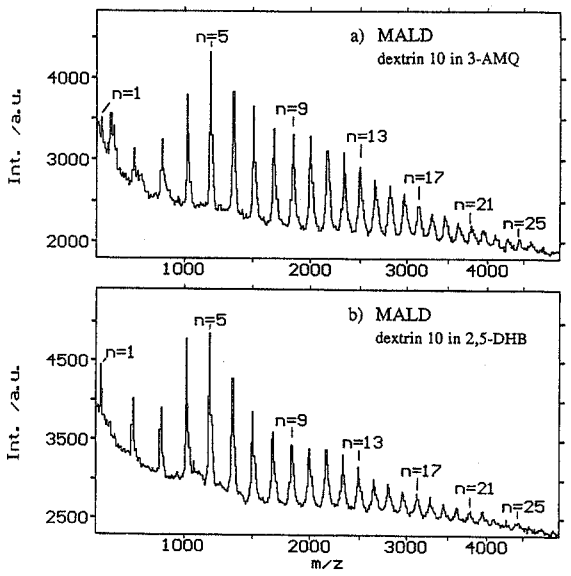

Fig. 7. MALD spectra of dextrin 10. (a) matrix: 3-aminoquinoline (3-AMQ), (b) matrix: 2,5-dihydroxybenzoic acid (2,5-DHB).

4. Conclusion

PDMS and MALD spectra of oligosaccharides obtained by the same time-of-flight spectrometer from samples, which were prepared by using a technique suitable for both methods, have been measured and compared. By comparing the spectra, the effect of different matrices assisting the production of polyatomic ions have been tested. Some heteroaromatic amines and phthaleins have been proven to be suitable matrices in PDMS as well as in MALD. Thus, matrices which enhance the quasimolecular ion intensity in PDMS, are also suitable MALD matrices when they absorb at the wavelength of the irradiating laser beam. Fluorescein, an excellent PDMS matrix for oligosaccharide analysis, has been successfully used as MALD matrix in the ultraviolet as well as in the visible spectral range. With regard to the observed matrix ions, the mass spectrum obtained by irradiating at 355 nm compare much better with the corresponding PDMS spectrum than that obtained by irradiating at 532 nm. Mass discrimination in the range from 500 to 1200 amu has been observed when applying MALD to samples prepared with equimolar mixtures of oligosaccharides or with dextrin 10. This result has been attributed to the fact that in MALD a large number of secondary ions, produced from a desorption area much larger than in PDMS, are competing with each other in the ionisation process. Raising the irradiance above the threshold, aggregate ions has been observed when using 3-aminoquinoline as MALD matrix. These ions are the result of specific reactions and possibly cationized anhydro-oligomers of the analytes.

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Contributions to *Section B* of *Nuclear Instruments and Methods in Physics Research* must be in English and should have an abstract. The manuscript and copies of figures should be submitted in duplicate, together with one set of good quality figure material (for production of the printed figures), to one of the Editors, Prof. H.H. Andersen or Dr. L.E. Rehn. Together with the manuscript an exactly identical electronic version on diskette can be submitted. Upon acceptance of the article for publication, both the manuscript and the diskette will be sent by the Editor to the Publisher. It is suggested that manuscripts originating from Europe, India, The Middle East and Africa be sent to Copenhagen and manuscripts from The Americas, The Far East and Australasia, to Argonne.

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[1] G.A. Smith, K.-H. Park, G.-C. Wang, T.-M. Lu and W.M. Gibson, Surf. Sci. 233 (1990) 115.
[2] T.Y. Tan, in: Defects in Semiconductors, eds. J. Narayan and T.Y. Tan (North-Holland, Amsterdam, 1981) p. 163.
[3] H. Yamazaki, Proc. 6th Int. Conf. on Ion Beam Modification of Materials, Nucl. Instr. and Meth. B 39 (1989) 433.

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