

Modification Induced by Alpha Particle Irradiation in Makrofol Polycarbonate

S. A. Nouh,¹ Amal Mohamed,² H. M. El Hussieny,¹ T. M. Hegazy³

¹Physics Department, Faculty of Science, Ain Shams University, Cairo, Egypt

²Physics Department, Faculty of Science, Zagazig University, Cairo, Egypt

³Physics Department, College of Girls, Ain Shams University, Cairo, Egypt

Received 30 August 2007; accepted 31 March 2008

DOI 10.1002/app.28469

Published online 27 May 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Makrofol DE 1-1 CC polycarbonate samples were exposed to alpha particles of initial energies at levels between 5.1 and 34 MeV. The modifications induced in polycarbonate samples due to the alpha particle irradiation have been studied through different characterization techniques such as X-ray diffraction (XRD), infrared spectroscopy, intrinsic viscosity, and color difference studies. The infrared spectroscopy indicated that the intensities of the characteristic absorption bands decrease with increasing the deposited alpha energy in the range 5.1–8.4 MeV, indicating that the degradation is the dominant mechanism at this range. At the same time, an increase in the –OH groups was observed at the same energy range 5.1–8.4 MeV due to the degradation of carbonate group and the

–H abstraction from the polymer backbone to form hydroxyl groups. The degradation reported by IR spectroscopy enhanced the degree of ordering in the degraded samples as revealed by XRD technique. Additionally, this degradation decreases the intrinsic viscosity from 0.56 to 0.43 at 35°C, indicating a decrease in the average molecular mass. The non irradiated Polycarbonate polymer is nearly colorless. It showed significant darkness sensitivity towards alpha particle irradiation, indicated by an increase in the color intercept L^* from 33.6 to 36.7. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 3447–3451, 2008

Key words: alpha; X-ray diffraction; IR spectroscopy; intrinsic viscosity; color; polymers

INTRODUCTION

Radiation modification of polymers is one of the modern methods, which enable the receiving of new polymeric materials with specific properties. Radiations cause a number of chemical changes in polymers, including crosslinking, chain scission, formation of C=C, formation of alkyne groups, depletion of heteroatoms, e.g., N, S, or O.^{1–5}

Radiation-induced modifications in polycarbonate have been studied extensively.⁶ The effect of radiation (electron, neutron, gamma rays, or ion beams) on polycarbonate is primarily chain scission. However, at increased energies, active sites or branching points created by scission may lead to intermolecular crosslinking. Methods to access the extent of radiation-induced changes in polymeric materials include mechanical testing (tensile strength, % elongation at break, compression testing, tear strength, puncture resistance), and physicochemical testing, i.e., thermal testing (measurement of changes in sealability or crystallinity), colorimetry (measurement of changes in color), IR spectroscopy (measurement of structural

changes), and rheological testing (i.e., measurement of changes in molecular weight).^{7–13} Also, the study of the color change in irradiated polymers is an important technique that has been used to assess physical and chemical changes in polymers. It is an important problem in commercial applications involving both the radiation processing of polymeric materials and the use of polymers in certain optical devices in radiation environments.¹⁴ This work reports some results on the structural and optical properties of Polycarbonate when irradiated with alpha particles of different energies. The aim is to investigate the modifications induced and analyze the effect as a function of the alpha particle energy.

EXPERIMENTAL

Samples

Makrofol DE 1-1 CC is a bisphenol-A polycarbonate with a chemical composition of $C_{16}H_{14}O_3$. It is manufactured by Farbenfabriken Bayer A.G., Leverkusen (Germany), with an average thickness of 300 μm and density 1.2 g/cm^3 . The functional groups of Makrofol aromatic polycarbonate include methyl, phenyl ring, carbonyl, ether, and hydroxyl.

Correspondence to: S. A. Nouh (samirnouh90@hotmail.com).

Irradiation facilities

The plastic samples were classified into two groups. The first group was exposed to a collimated beam of α -particles with initial energies 5.1 and 21.6 MeV using the U-120 Cyclotron of ZFK Rossendorf (Germany) with a fluence of 2×10^6 α -particles/cm² at normal incidence. The second group was exposed to energies of 9.6 and 34 MeV in the laboratory of nuclear research, Applied Nuclear Physics Research Center (Moscow) with the same conditions. The overall errors influence measurements are estimated to be $\sim \pm 8\%$.

Experimental apparatus

X-ray diffraction

The X-ray diffraction measurements were carried out with a Philips powder diffractometer type PW 1373 goniometer. The diffractometer was equipped with a graphite monochromator crystal. The wavelength of the X-rays was 1.5405 Å and the diffraction patterns were recorded in the 2θ range (4° – 80°) with scanning speed of 2° per minute.

Infrared spectroscopy

The infrared spectroscopic measurements were carried out using a Unicam SP1000 infrared spectrophotometer, which is a double beam, optical null, precision recording instrument. This instrument measures in the wavenumber range 400–4000 cm⁻¹, with wavenumber accuracy better than ± 3 cm⁻¹ over 400–2000 cm⁻¹ and better than ± 9 cm⁻¹ over 2000–4000 cm⁻¹.

Viscosity measurements

Solutions of different concentrations (0.2, 0.4, 0.6, and 0.8%) were prepared from the irradiated and non irradiated samples using pure chloroform as a solvent. The viscosity measurements were carried out in Oswald viscometer of the type pinkevitch Size 0 No. 2106, manufactured by Poulten, self, and LEE, LTD, England. This viscometer was calibrated in accordance with the standard method of test for kinematic viscosity specified in ASTM D 445-IP 71. The viscosity measurements were carried out at four different temperatures (35, 40, 45, and 50°C) using a bridge controlled thermostat bath E-270 Series III, Pownson, Oxford.

Color measurements

The transmission measurements were carried out using a Shimadzu UV-vis-Nir scanning spectrophotometer, type 3101 PC. This unit measures in the wavelength range from 200 to 3000 nm. The CIE

TABLE I

Values of the Initial Energies of Alpha Particles (E_{in}), the Range of Alpha Particles, the Energy Delivered Outside the Sample (E_{out}) and the Deposited Alpha Energy in the Polycarbonate Polymer (ΔE)

E_{in} (MeV)	Range (μm)	E_{out} (MeV)	ΔE (MeV)
5.1	32.176	0.000	5.100
9.6	86.767	0.000	9.600
21	325.280	4.332	16.668
34	760.22	25.608	8.392

(Commission International De E' Claire units x , y , and z) approach was used in the present work for the description of colored samples. The L^* , a^* , b^* intercepts used in this system are based on the CIE color triangle. In this system, the L^* value specifies the dark-white axis, a^* the green-red axis, and b^* the blue-yellow axis. The L^* , a^* , b^* intercepts of polycarbonate films were measured and taken as a reference. The color difference (ΔE^*) between the non irradiated sample and those irradiated with different alpha energies was calculated according to the CIE-LAB color-difference equation^{15,16}:

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

RESULTS AND DISCUSSION

Values of the range of alpha particles, the energy delivered outside the foil and the deposited alpha energy in the thin layer of the polymer were calculated using the stop pow (2000)-computer program by Henniger and are given in Table I.^{17,18} For absorber thicknesses through which the energy loss is not small, the deposited energy can be obtained in a way that makes use of range-energy data. The basis of the method is as follows: let R_1 represents the full range of the incident particle with energy E_0 in the absorber material. By subtracting the physical thickness of the absorber t from R_1 , a value R_2 is obtained that represents the range of those alpha particles that emerge from the opposite surface of the absorber. By finding the energy corresponding to R_2 , the energy of the transmitted charged particles E_t is obtained. The deposited energy ΔE is then given simply by $E_0 - E_t$.

It is noticed that there is a maximum energy deposited at 21 MeV, while it decreased at 34 MeV. This can be attributed to the fact that when alphas of higher energies fall on a thin material, most of the energy will be delivered outside the foil and only a small portion of the energy is deposited in the thin layer of the polymer.

X-ray diffraction

To study the effect of alpha particle irradiation on the degree of ordering in polycarbonate, X-ray dif-

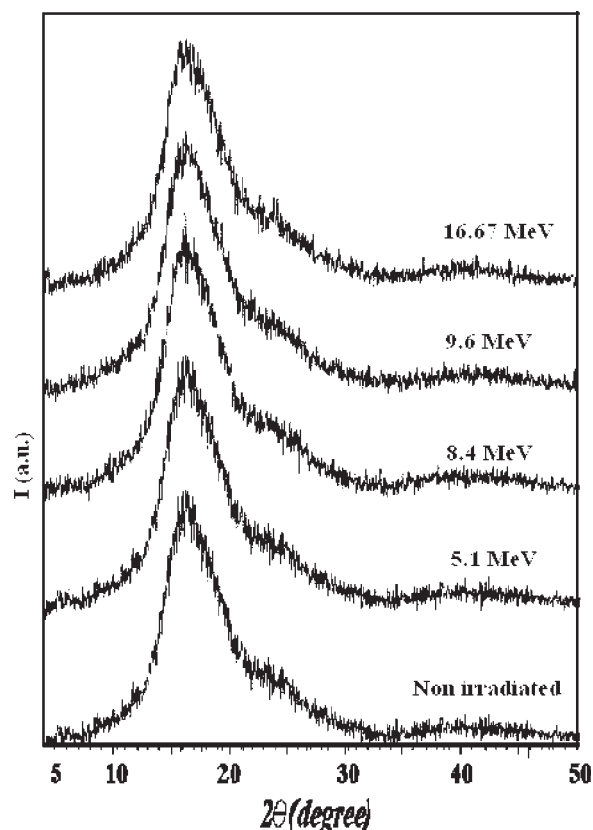


Figure 1 X-ray diffraction patterns of the nonirradiated and irradiated polycarbonate samples.

fraction measurements were carried out on solid state samples of 300 μm thickness. Figure 1 shows the X-ray diffraction patterns of the non irradiated and irradiated Polycarbonate samples. From the figure we see that the X-ray diffraction patterns of the samples were characterized by amorphous halos extending in the 2θ range 10° – 35° . The profile of the halos shows that the Polycarbonate polymer is an amorphous polymer with some ordering in it. Since the halo's width at the half of maximal intensity ΔW can give information about the presence of the ordering in the amorphous phase, approximate indicative values of ΔW were calculated and are given in Table II. Also, the area under the halos is proportional to the integral scattering intensity of the X-rays. The area under these halos (integral intensity) was calculated and approximate indicative values are given in Table II as a function of the deposited alpha energy. The results show that the irradiation with alpha particles in the range 5.1–8.4 MeV causes an increase in the ordering character in the amorphous phase of the polymer samples, which can be attributed to chain scission. Above 8.4 MeV and up to 16.67 MeV, the amount of ordering decreases, that could be attributed to the crosslinking which can decrease the ordering manner.

TABLE II
Values of Integral Intensity I , and Halo's Width at the Half of Maximal Intensity ΔW for Polycarbonate Samples as a Function of the Deposited Alpha Energy

Deposited alpha energy (MeV)	Integral intensity, I (a.u.)	Half width, ΔW (radian)
0.0	25.92	8.41
5.1	27.23	8.02
8.4	28.4	7.82
9.6	26.24	8.62
16.67	25.1	8.34

Infrared spectroscopy

The IR spectral analysis has been performed to investigate the structural changes induced in the polycarbonate polymer due to alpha particle irradiation. The changes have been estimated from the relative increase or decrease in the intensity of the peak associated to the functional groups present in the polymer. The material used in this study is aromatic polycarbonate. Its functional groups include methyl, phenyl ring, carbonyl, ether, and hydroxyl. The absorbance of different bands coming from the same function group exhibits the same trend with the deposited alpha particle energy. So, each characteristic group of polycarbonate is represented by only one wavenumber. Values of the absorbance of these absorption bands were calculated and plotted in Figure 2 as a function of the deposited alpha energy. From the figure it is clear that the absorbance measured at the wavenumbers 1778 and 889 cm^{-1} , decrease with increasing the deposited alpha energy up to 16.67 MeV, indicating the breaking of the C=O and C–O–C bonds. The absorbance meas-

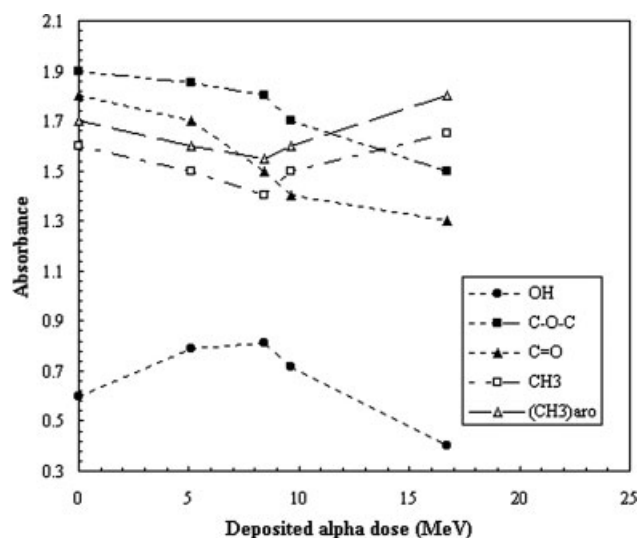


Figure 2 Variation of the absorbance, measured at the characteristic wavenumbers, with the deposited alpha energy.

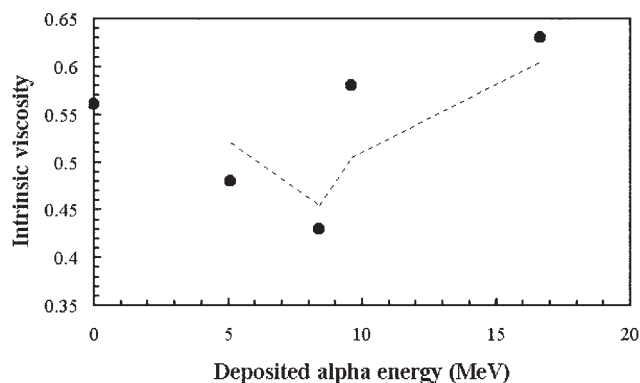


Figure 3 Variation of intrinsic viscosity with the deposited alpha energy.

ured at the wavenumber 2877 and 3047 cm^{-1} show a decrease in the intensity of C—H bond until a minimum value around the 8.4-MeV irradiated sample, followed by an increase on increasing the deposited alpha energy up to 16.67 MeV. The intensity of the peak corresponding to OH group (3533 cm^{-1}) increases with increasing the deposited alpha energy up to 8.4 MeV and then decreases with increasing the energy up to 16.67 MeV. These results indicate that scission takes place at the carbonate site with probable elimination of carbon dioxide/carbon monoxide and formation of hydroxyl group. The abstraction of —H may be from isopropyl or aromatic

group.¹⁹ The increase in the hydroxyl groups in the energy range 5.1–8.4 MeV which mean an increase in the end groups of macromolecules indicates that degradation process prevails in this energy range. Above 8.4 MeV and up to 16.67 MeV, an opposite trend has been observed due to the formation of bonds through crosslinking mechanism.

Intrinsic viscosity

Solutions of different loadings (0.2, 0.4, 0.6, and 0.8%) were prepared from the polycarbonate polymer using pure chloroform as a solvent. These diluted solutions were chosen to avoid any attractive secondary interactions between the polymer and solvent molecules which can be reflected in an increase of the viscosity in ways that accurate measurements cannot be made. The kinematic viscosity of the liquid samples can be calculated by the product of the observed time of flow and the capillary constant of the viscometer. The result is always expressed as relative viscosity (η_{rel}), calculated as the ratio of the viscosities of polymer solution and the pure solvent. Additional values may be calculated such as specific viscosity ($\eta_{\text{spc}} = \eta_{\text{rel}} - 1$), a reduced viscosity ($\eta_{\text{red}} = \eta_{\text{spc}}/\text{concentration}$) and intrinsic viscosity, the limiting viscosity number ($\eta_{\text{in}} = \lim \eta_{\text{red}}$ when the concentration tends to zero) that is related to the aver-

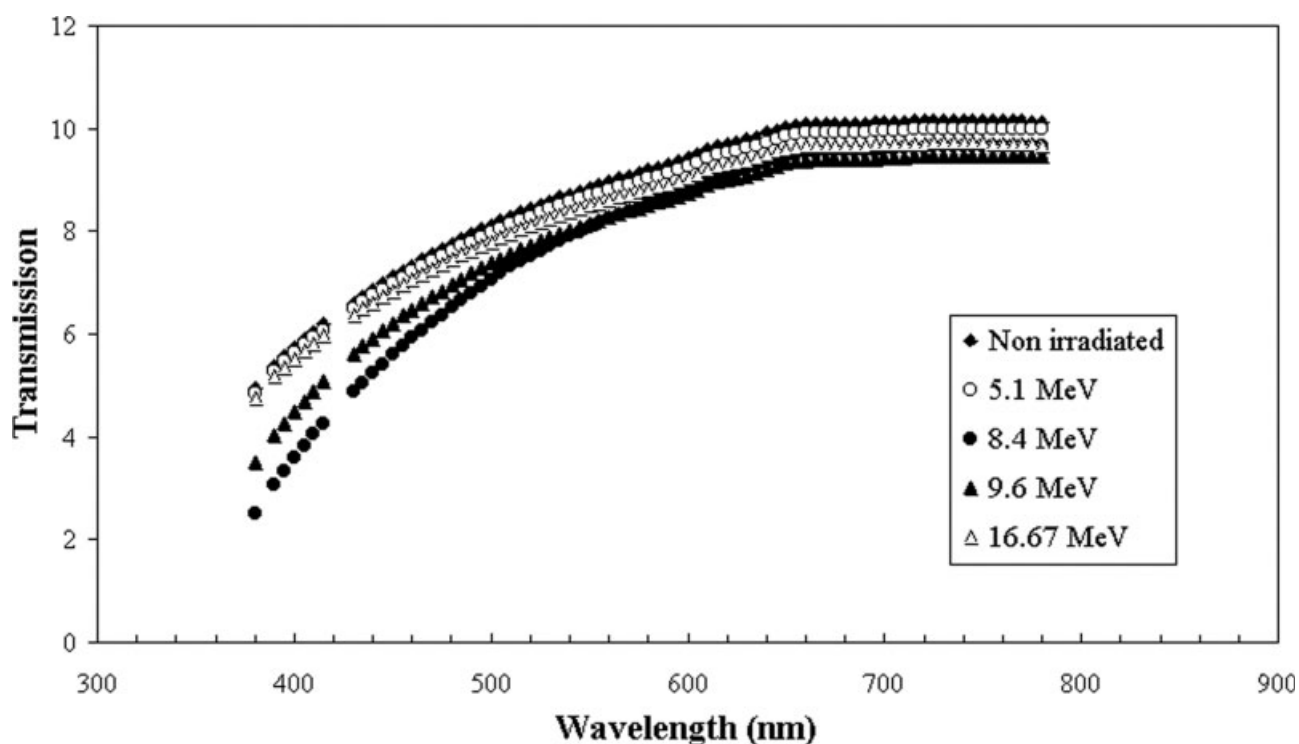


Figure 4 The transmission spectra of the non irradiated and irradiated polycarbonate samples measured in the wavelength range 380–780 nm.

TABLE III
The Color Intercepts (L^* , a^* , and b^*) and Color Intensity ΔE^* of Polycarbonate Samples as a Function of the Deposited Alpha Energy

Deposited alpha energy (MeV)	Color intercepts			ΔE^*
	L^*	a^*	b^*	
0	33.6	0.52	3.6	0.00
5.1	33.9	0.50	3.4	0.52
8.4	34.4	0.48	3.7	0.51
9.6	35.8	0.49	3.6	0.54
16.67	36.7	0.51	3.4	0.59

age molecular mass of the dissolved polymer. The intrinsic viscosity of the polycarbonate liquid samples could be measured at 35°C. Figure 3 shows the variation of intrinsic viscosity of polycarbonate samples with the deposited alpha energy. From the figure it is clear that the intrinsic viscosity decreases until a minimum value around the 8.4-MeV irradiated sample and then increases on increasing the deposited alpha energy up to 16.67 MeV. The energy range in which the intrinsic viscosity decreases can be explained by the formation of shorter molecules as a result of degradation which causes both a random breaking of bonds and the formation of stable molecules with a lower molecular weight. While the increases in intrinsic viscosity in the energy range 8.4–16.67 MeV, indicates an increase in the molecular mass of the polymer due to crosslinking process.

Color changes

The transmittance of the non irradiated and irradiated polycarbonate samples, in the wavelength range 380–780 nm, was measured and is shown in Figure 4. The color intercepts (L^* , a^* , and b^*) and the color difference ΔE between irradiated and non irradiated polycarbonate samples were calculated and are given in Table III. The accuracy in measuring (L^*) is ± 0.2 and ± 0.1 for (a^* and b^*). It can be seen that the color parameters (a^* , b^* , and ΔE) were not changed after exposure to alpha particles, means that the green ($-a^*$) and blue ($-b^*$) color components of the non irradiated film were not affected by the alpha energies. This is accompanied by an increase in the darkness of the samples (L^*). This increase in darkness can be attributed to the trapping of the excited free radicals that are formed by ionization.¹⁴

CONCLUSIONS

The alpha particle irradiations of Polycarbonate polymers lead to chain scission followed by crosslinking and as a result there are changes in its structural, molecular, mechanical, and optical properties.

The degree of ordering in polycarbonate was found to be dependent on the deposited alpha energy. The irradiation of polycarbonate at the energy range 8.4–16.67 cause crosslinking which reduces ordering and increases the amorphous regions that enhance polymer toughness. Thus this polymer may be suitable candidate for industrial application requiring it's bending without breaking.

Infrared measurements show that the carbonyl group (C=O) degrade under alpha particle irradiation in the studied energy range, which shows that the carbonyl groups are the most sensitive groups to alpha irradiation.

The intrinsic viscosity and thus the average molecular mass of the polycarbonate polymer were found to be dependent on the deposited alpha energy due to the chain scission and crosslinking mechanisms. Thus, the alpha particles irradiation effects on the intrinsic viscosity of polycarbonate polymer may be considered as a simple way to optimize its quality since the processing and application properties of that polymer depend very largely on its molecular structure.

The non irradiated Polycarbonate polymer is nearly colorless; however, it showed significant darkness sensitivity towards alpha particle irradiation.

References

1. Marletta, G. Nucl Instrum Methods B 1990, 46, 295.
2. Calcagno, L.; Compagni, G.; Foti, G. Nucl Instrum Methods B 1992, 65, 413.
3. Balanzat, E.; Bouffard, S.; Bouquerel, A.; Fuess, H.; Trautmann, C. Nucl Instrum Methods B 1996, 116, 159.
4. Steckenreiter, T.; Balanzat, E.; Fuess, H.; Trautmann, C. Nucl Instrum Methods B 1997, 131, 159.
5. Mujahid, M.; Singh, P.; Srivastava, D.; Shiuli, G.; Avasthi, D.; Kanjilal, D. Radiat Meas 2004, 38, 197.
6. Ferain, E.; Legras, R. Nucl Instrum Methods B 1993, 82, 539.
7. Kabeel, M.; Sokkar, T.; Shahin, M. Radiat Phys Chem 1991, 38, 199.
8. Nouh, S. A.; Abdel-Naby, A. Radiat Eff Defects Solids 2007, 162, 109.
9. Thorat, H.; Prabhu, C.; Sureshkumar, K.; Pandya, M. J Appl Polym Sci 1995, 59, 1769.
10. Demertzis, P.; Franz, R.; Welle, F. Packag Technol Sci 1999, 12, 119.
11. Jahan, M.; King, M.; Haggard, W.; Sevo, K. L.; Parr, J. Radiat Phys Chem 2001, 62, 141.
12. Hassanpour, S.; Khoylou, F. Nucl Instrum Method B 2003, 208, 358.
13. Goulas, A.; Riganakos, K.; Kontominas, M. Radiat Phys Chem 2004, 69, 411.
14. Nouh, S. A.; Morsy, A.; El-Hussieny, H. Radiat Eff Defects Solids 2004, 159, 115.
15. Nassau, K. Color for Science, Art, and Technology; Elsevier: New York, 1998.
16. Hossam, M.; Ali, Z.; Hussein, E. J Appl Polym Sci 2006, 101, 4358.
17. Nouh, S. A.; Wahab, L. A.; Eissa, H. M. Radiat Meas 1998, 29, 465.
18. Nouh, S. A.; Gaafar, S. A.; Eissa, H. M. Phys Stat Sol A 1999, 175, 699.
19. Srivastava, A.; Singh, T. V.; Mule, S.; Rajan, C. R.; Ponrathnam, S. Nucl Instrum Methods B 2002, 192, 402.