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FTIR and FT-Raman Spectroscopic Study on Polymer Based High Pressure Digestion Vessels

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Surface corrosion of polytetrafluoroethylene (PTFE) based microwave digestion vessels was monitored by reflection FTIR and FT-Raman techniques. Samples were taken from digestion vessels after 0 (new), 50, 100, and 200 digestion cycles of milk powder. The spectrum of the new (unused) sample was subtracted from the spectra of used vessels in order to identify small differences, *e.g.,* surface degradation or modification, between the samples. The new IR features of CF_2 and CF_3 groups for PTFE samples at 1197, 1139, and 642 cm^{-1} refer to surface modification (degradation) of the polymer chain. Special surface species, such as aliphatic hydrocarbons, inorganic nitrates and FNO_3, were identified. The Raman spectra of PTFE samples also showed formation of new CF_3 groups, indicating that the polymer chain (or side chain) was changed (shortened) after different cycles.

Keywords
surface degradation
FTIR micro ATR
FT-Raman
Teflon digestion vessel

INTRODUCTION

In trace analysis, even element concentrations lower than 100 ng/g are determined in organic and inorganic samples. Even at pg/g (10^{-12} g/g), trace elements can be determined with high accuracy and precision by using proper analytical techniques.[1] Absolute and relative detection limits can be extended and the scope of the determination technique can be widened by decomposition (destruction) of the sample and/or enrichment (preconcentration) of the desired trace elements prior to the determination. The most commonly used decomposition process is the closed vessel high-pressure digestion.[2,3] Many biological and geological samples, minerals and marine sediments can be successfully digested in Teflon-lined steel bombs with concentrated HNO_3, *aqua regia*, a HNO_3-HCl-HF mixture, *etc*. High-pressure asher, performed in a steel digestion bomb with pure quartz or carbon glass inner surface

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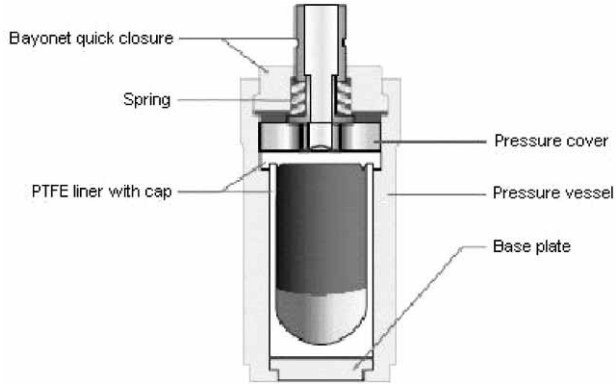

Figure 1. Cross-section of a PTFE based high pressure digestion vessel.

materials, can be successfully applied, besides environmental and biological samples, also for ceramic materials or noble metals.[4] Microwave digestion is the latest decomposition process, applicable to closed-vessel techniques, since solutions may be heated directly in low-conductivity microwave-transparent vessels (quartz, Teflon). The cross-section of a Teflon based high pressure digestion vessel is shown in Figure 1.

Reproducibility and accuracy of analysis strongly depends on surface purity and inertness of the digestion vessel. Sample material loss due to adsorption on the digestion vessel, diffusion in the micropores, and also sample contamination due to desorption of impurities from the vessel surface (memory effect) may cause systematic errors. Such interactions with the vessel wall might even become a limiting factor in ultratrace determinations at the (ng/g)-level and below, *e.g.*, in environmental control or in quality assurance of foodstuffs or pharmaceuticals. Therefore, investigations of surface morphologies and surface structural changes for decomposition vessels used in digestion systems are increasingly gaining on importance.[5,6] Recently, FT-Raman spectroscopy was applied to surface characterization of fused quartz vessels. The onset of recrystallization was detected much earlier by the FT-Raman method than by morphological changes in scanning electron microscopy.[7]

A similar attempt was made at monitoring inner surface corrosion of fluorinated polymer-based microwave digestion vessels by FTIR and FT-Raman techniques. It was assumed that the inner wall surface of the polymer-based digestion vessels undergoes significant changes during several cycles of use. Since the samples (pieces from the digestion vessel walls) are very thick and often have a concave shape, such experimental infrared techniques as transmission, emission or diffuse reflection methods cannot be readily applied. Reflection methods were found suitable for recording infrared spectra of surfaces and especially the attenuated total reflection (ATR) method produced very good quality spectra of plastic samples. Raman spectroscopy has not attracted much attention of surface scientists, although this method combines several advantages in a unique way. Recently, it is gaining on importance in surface studies of layered and/or crystallized structures.[8]

EXPERIMENTAL

Material for investigated digestion vessels was polytetrafluorethylene modified with 0.2 0 to 0.5 % perfluorovinyl ether (PTFE-TFM). Addition of small quantities (less than 1 %) of perfluorovinyl ether does not affect the chemical, thermic or electric properties of PTFE; however, processing by sintering and pressure application becomes easier, resulting in a flatter surface of reduced permeability.[6]

Samples were taken from digestion vessels after 0 (new), 50, 100, and 200 digestion cycles of 0.2 g milk powder and 4 ml 65 % HNO_3 at a 30 bar pressure and 180 °C for 30 min in a Multiwave microwave digestion system (Anton Paar and Perkin Elmer). Square-shaped (≈1x1 cm) sample pieces were cut out from the wall with a band-saw.

A »Golden Gate« ATR accessory adapted to the Varian (Digilab) FTS-135 spectrometer was used for reflection measurements on polymer-based digestion vessels. The ATR optical element is a small 2x2 mm diamond ATR unit brazed into a tungsten carbide mount. The active area of the diamond crystal is 0.6 x 0.6 mm. The angle of incident light is 45° and it operates in a single reflection mode. Specific anvils with the top sapphire clamp mechanism provide the necessary pressure to flatten the concave inner surfaces of the digestion vessel samples (1x1 cm). An empty diamond ATR unit was used for recording the reference spectra. 16 scans were made at a resolution of 4 cm^{-1} for spectral accumulation in every measurement.

FT-Raman spectra were recorded by means of a Varian (Digilab) dedicated FT-Raman spectrometer (Nd-YAG laser, 1064 nm, 500 mW laser power) and corrected to the white light background. 1024 spectra were averaged in order to improve the signal to noise ratio.

RESULTS AND DISCUSSION

General Assignment of the PTFE-TFM Polymer Spectrum

Infrared (ATR) and Raman spectra of the PTFE-TFM wall sample after 200 digestion cycles are shown in Figure 2.

The proposed assignments (Table I) were made on the basis of the general formula of PTFE: $-[-CF_2-CF_2-]_n-$.

Dominant IR bands at 1299, 1199, 1146, 715–774, 553, 507 cm^{-1} and Raman bands at 1296, 735, 386, 291 and 202 cm^{-1} belong to the different modes of CF_2 groups.[9–11] Weak IR bands at 2960, 2927, 2853 (CH_2, CH_3 stretching mode) and 1438 cm^{-1} (CH_2, CH_3 deformation) as well as the Raman band around 2900 cm^{-1} (CH_2, CH_3 stretching) belong to surface hydrocarbons formed on the surface of the vessel wall during digestion cycles.

TABLE I. IR and Raman band assignments of the PTFE vessel wall sample after 200 digestion cycles

IR bands	Raman bands	Assignment
2960 vvw		
2927 vw	≈2900 vw, b	CH_2, CH_3 stretching[a]
2853 vw		
1458 vw		CH_2, CH_3 deformation[a]
	1379 m	CF stretching
1360 vvw		NO_3^- (nitrate)[a]
1299 vw, sh	1296 m, w	CF_2 asymmetric stretching
	1213 w	CC stretching
1199 vs		CF_2 symmetric stretching
1146 vvs		
	1084 vvw	CF_3 symmetric stretching
	735 vvs	CF_2 symmetric stretching[b]
774 w		
729 w		CF_2 scissoring
720 w		
715 vw, sh		
640 m		CF deformation
630 m		
	594 w	CF_3 symmetric deformation
	571 w	(umbrella)
553 m		CF_2 bending
507 s		
	386 s	CF_2 twisting
	291 s	CF_2 wagging
	202 vw	CF_2 rocking

[a] Marked band assignments belong to species formed on the surface of the vessel wall during 200 digestion cycles.

[b] Assigned to A_1 mode, involving symmetric C–F and C–C stretching modes.[11]

The CF stretching and bending modes can be characterized by 1379 cm^{-1} Raman and 640, 630 cm^{-1} IR bands, respectively. Bands at 640 and 630 cm^{-1} are assigned in the literature as belonging to groups located in the crystallized zones of PTFE polymer.[10] In the literature, the weak Raman 594 and 571 modes are assumed to be due to a defect in the Teflon structure.[11] In our opinion, these bands belong to CF_3 groups (CF_3 symmetric deformation mode) along with the very weak peak at 1084 cm^{-1} (CF_3 symmetric stretching mode).

At first sight, traces of aliphatic hydrocarbons and NO_3 groups can be detected as very weak bands at 1458 and 1360 cm^{-1}, respectively, as a result of surface reactions or adsorption. In order to obtain fine spectral differences between samples, it is reasonable to produce difference spectra, *i.e.*, to subtract the spectrum of the new unused vessel sample from those of samples representing different numbers of digestion cycles.

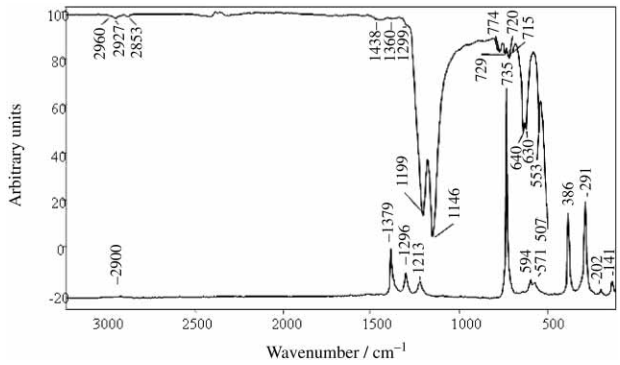

Figure 2. Infrared (upper trace) and Raman (lower trace) spectra of the PTFE-200 vessel wall sample.

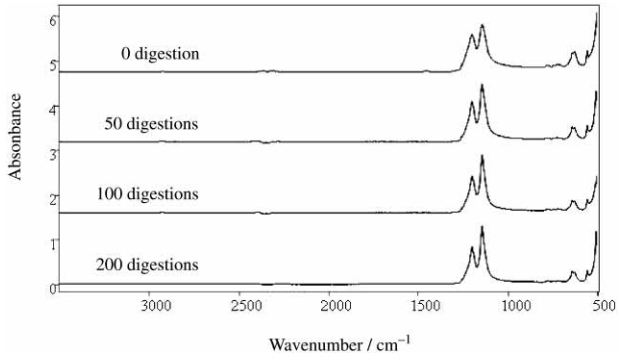

Figure 3. ATR spectra of PTFE-TFM samples treated with HNO_3 at ≈180 °C in a different number of digestions (0, 50, 100 and 200 digestions).

ATR Spectra of PTFE Vessel Wall Samples

Reflection spectra of internal surface of the PTFE vessel wall are presented in Figure 3. The spectra of used vessels for 0 (new), 50 (PTFE-50), 100 (PTFE-100) and 200 (PTFE-200) digestion cycles seem to be very much the same. Maximum intensity of the band at 1146 cm^{-1} is about 1.5 absorbance unit (A).

To identify small differences between the samples, the spectrum of the starting new PTFE sample was subtracted from the other three spectra. The difference spectra are presented in Figure 4. It can be seen that the spectral differences fall in the range of 0.1 absorbance unit (A) or less. Only three positive new bands were detected for the PTFE-50 sample at 1197 (m), 1139 (s) and 642 (w) cm^{-1}. These spectral changes can be explained by definite modifications of the polymer chain or side group; bands belong to CF_2 and CF groups.

Rather well defined aliphatic hydrocarbon bands were observed at 2926, 2853 and 1448 cm^{-1} for the PTFE-100 sample. These bands can originate from the milk powder

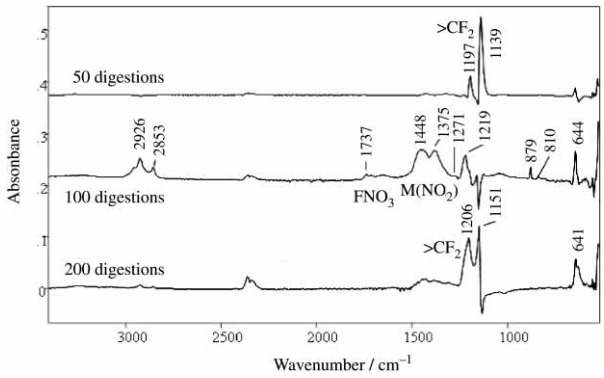

Figure 4. Difference spectra obtained by subtraction of the reflection spectrum of the unused PTFE-TFM wall sample from the spectra of used wall samples.

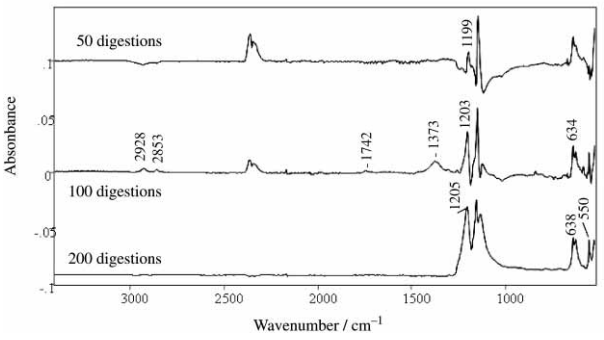

Figure 5. Difference spectra obtained by subtraction of reflection spectra of the new PTFE-TFM sample (bottom) from the spectra of used samples.

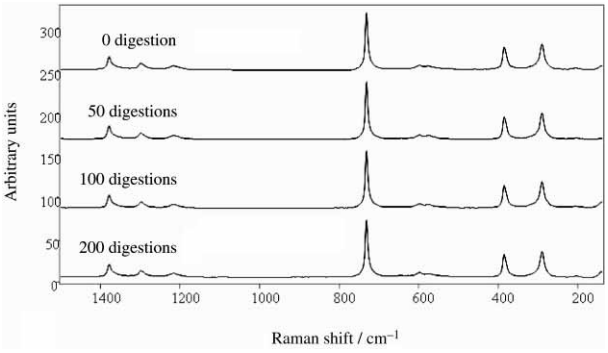

Figure 6. FT-Raman spectra of PTFE-TFM vessel wall samples.

decomposition. Further digestion procedures remove these hydrocarbon traces from the surface. Only very weak features in the CH stretching region are detectable for the PTFE-200 sample (Figure 4, bottom spectrum). Strong bands at 1375 and 879 cm^{-1} can be assigned to inorganic nitrates while weak bands at 1737, 1271 and 810 cm^{-1} can be attributed to the surface FNO_3 compound. In gaseous state, FNO_3 has strong bands at 1755, 1297 and 804 cm^{-1}.[12] Intense new bands at 1219 and 644 cm^{-1} refer to structural changes of the PTFE polymer, as interpreted for the PTFE-50 sample.

Surprisingly, less spectral difference was observed in the ratio spectrum of the PTFE-200 sample (Figure 4, bottom spectrum). However, this is in agreement with the corrosive effects and layered launching observed on the vessel wall after 200 digestion cycles during morphological investigations.[6] Weak bands attributed to inorganic nitrates and aliphatic hydrocarbons are still observable close to the positions obtained for the PTFE-100 sample. Again, the strongest and uncommon bands at 1206, 1151 and 641 cm^{-1} are due to structural changes in the polymer chain or in the side chain group.

ATR Spectra of PTFE Vessel Bottom Samples

Subtracted spectra of PTFE vessel bottom samples are presented in Figure 5. The general pattern is similar to those obtained earlier for cylindrical wall samples. However, SEM measurements showed that even in the case of new vessels the bottom surface was more damaged compared to the vessel wall.[6]

Intensive difference bands around 1200 and 600 cm^{-1} indicate a slightly higher degradation of the TFE polymer in bottom samples. The more intensive band at 550 cm^{-1} belongs to the asymmetric deformation mode of CF_3 groups; consequently, the relative amount of the end CF_3 groups increases with the increased number of digestion cycles.

Similarly to sidewall samples, various surface species (FNO_3, inorganic nitrates, hydrocarbons) were detected for bottom sample as well. Relative intensities are lower in this case.

Raman Spectra of PTFE Samples

The Raman spectra of vessel wall samples after different cycles of use are shown in Figure 6. No real differences can be obtained in the plotted form for a certain scale expansion. In this case, spectral information comes from a thinner surface (around 0.5 mm), function of the wavelength of the excitation laser (1064 nm). (Penetration depth of the ATR measurements is around 1–2 μm.) Spectral differences are plotted in Figure 7. The only »positive« band related to the species formed during the digestion

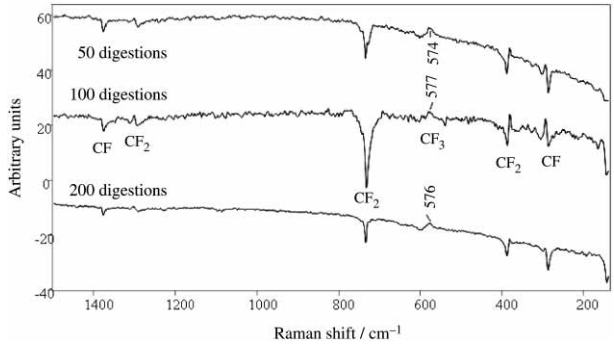

Figure 7. Raman difference spectra of PTFE-TFM vessel wall samples.

procedure is about 570 cm^{-1}, assigned to the symmetric deformation (umbrella) mode of the CF_3 group. The so-called »negative« bands belong to the diminishing structures, namely to CF and CF_2 groups. All these spectral observations lead to the conclusion that the polymer chain (or side group) has been shortened, *e.g.,* »broken«, leading to the formation of more and more CF_3 end groups.

CONCLUSIONS

ATR FTIR spectra of the used PTFE vessels have shown a definite surface degradation of the fluorinated polymer. Formation of surface hydrocarbons, deposition of inorganic nitrates and formation of the FNO_3 compound as a surface species were recorded. From the Raman spectra of the same samples, it can be concluded that the polymer chain has been shortened as a result of the formation of CF_3 end groups.

Morphological changes of surfaces were monitored by scanning electron microscopy as well,[6] but the above discussed speciation of surface modifications and identification of chemisorbed species can be done only by molecular spectroscopic methods. Reflection FTIR and FT-Raman spectroscopy proved to be excellent tools for understanding surface degradation and surface reactions in polymer-based digestion vessels.

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SAŽETAK

Istraživanje polimernih posuda za visokotlačno razaranje pomoću FTIR i FT-Ramanove spektroskopije

Judith Mihály, Silvana Sterkel, Hugo M. Ortner, László Kocsis, László Hajba, Éva Furdyga i János Mink

Površinska korozija posude za mikrovalno razaranje od polimera tetraflouroetilena (PTFE) praćena je refleksijskim tehnikama FTIR i FT-Raman. Uzorci su uzeti sa posuda za mikrovalno razaranje nakon 0, 50, 100 i 200 ciklusa razaranja mlijeka u prahu. Spektar novog uzorka oduzet je od spektara korištenih posuda s ciljem utvrđivanja malih razlika, primjerice površinske razgradnje ili promjena, između uzoraka. Karakteristike vibracija skupina CF_2 i CF_3 pri 1197, 1139 i 642 cm^{-1} upućuju na površinsku promjenu polimernog lanca. Identificirane su posebne površinske specije kao što su alifatski ugljikovodici, anorganski nitrati i FNO_3. Ramanovi spektri uzoraka PTFE pokazali su nastajanje novih CF_3 skupina, što upućuje na promjene (smanjivanje) polimernih (ili bočnih) lanaca nakon različitih ciklusa.