Short communication

A Novel Analytical Technique Suitable for the Identification of Plastics

Marijan Nečemer,[1,*] Peter Kump,[1] Primož Šket,[2,4] Janez Plavec,[2,4,5] Jože Grdadolnik[2,4] and Maja Žvanut[3]

[1] *"J. Stefan" Institute, Jamova 39, 1000 Ljubljana, Slovenia*

[2] *National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana*

[3] *National Museum of Slovenia, Prešernova 20, 1000 Ljubljana*

[4] *EN-FIST Centre of Excellence, Dunajska 156, 1000 Ljubljana*

[5] *Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5, 1000 Ljubljana*

* *Corresponding author: E-mail: marijan.necemer@ijs.si*

Received: 20-12-2012

Abstract

The enormous development and production of plastic materials in the last century resulted in increasing numbers of such kinds of objects. Development of a simple and fast technique to classify different types of plastics could be used in many activities dealing with plastic materials such as packaging of food, sorting of used plastic materials, and also, if technique would be non-destructive, for conservation of plastic artifacts in museum collections, a relatively new field of interest since 1990. In our previous paper we introduced a non-destructive technique for fast identification of unknown plastics based on EDXRF spectrometry,[1] using as a case study some plastic artifacts archived in the Museum in order to show the advantages of the nondestructive identification of plastic material. In order to validate our technique it was necessary to apply for this purpose the comparison of analyses with some of the analytical techniques, which are more suitable and so far rather widely applied in identifying some most common sorts of plastic materials.

Keywords: EDXRF; FTIR, NMR, plastics characterization;

1. Introduction

Plastics are man made long chain polymeric molecules.[2] More than half a century ago synthetic polymers started to substitute natural materials in almost every area, and nowadays plastics have become an indispensable part of our life. Plastics and rubbers are found also in a variety of museum collections; historic, ethnographic, scientific, and design, as well as in modern and contemporary art. Since their rapid development during the first half of the 20th century, plastics have been infiltrated into the every aspect of modern daily life.[3]

Many instrumental methods are suitable for identification and analysis of plastics and additives such as mass spectrometry (MS),[4,5] infrared spectrometry (IR),[6–8] nuclear magnetic resonance (NMR),[9–11] Raman spectrometry (RS),[12,13] inductively coupled plasma mass spectrometry (ICP-MS),[14] inductively coupled plasma-optical emission spectrometry (ICP-OES),[15] energy dispersive X-ray fluorescence spectrometry (EDXRF), [17–19] total reflection X-ray fluorescence spectrometry (TXRF),[20,21] atomic absorption spectrometry (AAS),[15,22] laser-induced breakdown spectrometry (LIBS)[23] etc. These methods are mainly applicable for industrial and laboratory purposes, where the sample under investigation could be destroyed, decomposed by chemical reagents, and then analyzed for its chemical composition. In case of preservation and restoration of plastic artifacts, destructive analytical methods are usually out of question due to certain damage to artifacts, which are in most cases fragile, which leads to their permanent loss. In recently published article[1] we introduced the EDXRF technique and reported some of the preliminary results on plastic identification. In that work a non-destructive simple analytical protocol for identification of various plastic materials based on the index of incoherent/coherent scattering of Cd-109 on plastic samples was presented. In that study the detailed physics background of the approach, such as calibration procedure and treatment of EDXRF results was explained, applying also the multivariate statistical method. In present work the aim is to validate the introduced new EDXRF analytical technique and the respective protocol, and to apply therefore for this purpose the comparison with the analytical techniques such as Fourier Transform Infrared spectroscopy and solid state Nuclear Magnetic Resonance for a set of most common sorts of plastic materials.

2. Experimental

2. 1. Sampling and Semi-destructive Sample Preparation for FTIR and NMR

For this purpose a fine iron file was used to grind off plastic material from the object in the form of powder. It was found that this sampling protocol was simple and fast; the powder sample removed was homogeneous and suitable for further analysis with FTIR and NMR. After sampling the file was cleaned with a paint brush to remove traces of sample in order to avoid cross-contamination beetwen the samples under investigation.

2. 2. FTIR

The infrared spectra were measured with a Bruker Vertex FT infrared spectrometer using a single reflection ATR cell (Specac) equipped with a Type IIIA monolithic diamond and KRS-5 lenses. Spectra were recorded at room temperature in the range between the 7000 cm^{-1} and 370 cm^{-1}.[24] A liquid nitrogen cooled MCT detector was used. Typically 256 scans were recorded, averaged and apodized with the Happ-Genzel function. The spectrometer was purged with dry nitrogen during measurements, which were made using an appropriate amount of solid sample covering the whole diamond surface (~. 1.5 mm^2). Optimal contact between sample and diamond was ensured by the sapphire self-leveling pressure anvil. Spectra were used as recorded; no additional spectral corrections were applied.

2. 3. NMR Spectroscopy

The powdered sample particles were packed in the 5 mm rotor (volume 110 μL) as uniformly as possible using a packing tool and compressed as much as possible.

NMR spectra of solid samples were recorded on a Varian Unity Inova 300 MHz NMR spectrometer equipped with a 5 mm Magic Angle Probe.[25] The Larmor frequencies of protons and carbon nuclei were 302.98 MHz and 76.19 MHz, respectively. The ^{13}C CP-MAS NMR spectra were externally referenced using hexamethylbenzene (HMB). All samples were spun at the magic angle with a 5 kHz spinning frequency. The pulse sequence used for acquiring the ^{13}C CP-MAS spectra was a standard cross-polarization MAS pulse sequence with high-power proton decoupling during acquisition. The repetition delay in all experiments was 5 s and the number of scans was between 3700 and 29500, depending on the signal-to-noise ratio.

2. 4. EDXRF

Samples of the same plastic materials were also analyzed non-destructively by EDXRF. Fluorescent radiation was excited in the samples by a disc radioisotope excitation source of Cd-109 (10 mCi) from Isotope Products Laboratories, U.S.A. The spectra were measured by the Si(Li) detector (Ortec EG&G) attached to the preamplifier, amplifier (Canberra M2025), ADC (Canberra M8075), and a PC- based MCA (S-100, Canberra). The coherent and incoherent scattered lines of the excitation source (Ag K_α) were also recorded in the X-ray spectrum and used in the analytical procedure. The complete description of the EDXRF analytical approach of plastic materials was in detail presented in our previous work.[1]

In polymer samples, the matrix is mainly made up of carbon, oxygen and hydrogen, which due to its low average atomic number do not contribute to the detected fluorescence, but mainly to prominent scattered lines of the exciting radiation (incoherent-inelastic and coherent-elastic).[1,20,21]

A simple classification model [1] based on parameters obtained from the scattered radiation measured from samples of plastic materials of known chemical composition was constructed. For this purpose a random set of 30 samples of various plastics which were available in the store

Table 1. Results of calibration (calculated N_{inc}/N_{coh} and Z*) of EDXRF system with samples of known polymer type.

Type of plastic	N_{inc}/N_{coh}	Z*
Polyethylene (PE)	34.4–35.2	5.81–5.96
Polypropylene (PP)	29.4–31.0	6.03–6.23
Polyamide (PA, Nylon 66)	23.1–26.2	6.52–6.95
Polymethyl methacrylate (PMMA, Plexiglas)	18.0–18.9	7.40–7.54
Polyethylene terephthalate) (PET)	15.0–15.1	8.08–8.10
Phenol formaldehyde resins (PF, Bakelite)	11.5–13.6	8.41–8.98
Styrene butadiene styrene (SBS)	11.7–12.0	8.92
Polytetrafluoroethylene (PTFE, Teflon)	8.54–8.98	9.88–10.10
Polyvinyl chloride (PVC)	8.08–8.77	9.98–10.30

of the institute workshop were chosen . The plastics were traceable via certificates and/or production origin. Among them were phenol-formaldehyde resin (PF, Bakelite, 5 samples), polyethylene (PE, 5 samples), polypropylene (PP, 5 samples), polyvinylchloride (PVC, 2 samples), polymethylmethacrylate (PMMA, Plexiglas, 2 samples), polytetrafluoroethylene (PTFE, Teflon, 3 samples), polyamide (PA, 5 samples), polyethyleneterephthalate (PET, Mylar, 2 samples), and styrene-butadiene-styrene (SBS, 1 sample) were selected for analysis. All the mentioned samples were directly measured and the spectra were analyzed for the scattered lines and also for the fluorescent lines of elements present in the plastics as additives such as Ca, Ti, Zn, Sr etc. In this way, the ratios between incoherent and coherent peaks, N_{inc}/N_{coh}, as well as the respective Z* (average effective atomic number)[1] for each type of plastic used for calibration were calculated. In Table 1, the calculated N_{inc}/N_{coh} ratios and Z* values for selected plastics of known type and composition used as calibration of the EDXRF system[24] are shown.

3. Results and Discussion

The proposed identification procedure can be applied in the fields of industrial quality control of plastics for purpose of sorting the used plastics for further reproduction, and also for non-destructive identification of plastic museum artifacts. In our case aimed at validation of the EDXRF approach some artifacts from the museum collection were used in order to show that nondestructive identification of plastic material by the fast and rather simple technique is possible. The unknown polymer type of the artifacts under investigation was preliminarily determined in the above mentioned model by EDXRF and to validate it the semi-destructive FTIR and solid state NMR (CP-MAS) analyses were applied to the same samples. In Table 2, the respective comparison of the results is presented.

The above described samples were named according to its shape and usage like toys, goggles, souvenirs etc. The NMR and FTIR analyses revealed that some plastic artifacts were produced from a mixture of plastics, or by the addition of minor amounts or traces of other types of plastics to the major component. Thus, samples 1 and 2 were identified as mixtures of different plastics (PS, PF, SBS or even ABS), while sample 5 (PE + addition of minor PA), sample 7 (PVC + addition of unknown aromatic-based additives), and sample 3 (PS + contained additions of PVC); other samples were more or less produced from one compound. The NMR and FTIR techniques were obviously more sensitive for identification of plastics than EDXRF.

It was evident that the proposed EDXRF model was quite efficient for the identification of unknown plastics among the selected plastic artifacts. Sample 1, 2, 5 and 8 were classified by FTIR and NMR as a mixture of basic polymers. In the case of 1, PS was identified by FTIR and PF by NMR, but EDXRF identified it as SBS or PF; identification by NMR and EDXRF in this case coincided. In case 2, PS or ABS were classified by FTIR, PS or SBS by NMR, PF or SBS by EDXRF. Identification of PF by EDXRF looks critical. In case 3, PS was classified by FTIR and NMR, PF or SBS by EDXRF. The identification was correct in all three cases since SBS and PS represent the same type of plastic based on the styrene matrix. In the case of sample 5 EDXRF classification gave PP, whereas FTIR and NMR both gave PE. Also NMR measurement showed a minor content of PA in this sample. The reason for the EDXRF classification as PP was probably due to addition of a minor content of PA to this sample which obviously decreased its N_{inc}/N_{coh} ratio, causing it to fall into the lower PP region (see Table 1). The EDXRF identification of sample 10 was PA, whereas FTIR and NMR classified this sample as PS.

The overall correct classification of 11 plastic artifacts by the EDXRF model was approximately 80%, which was quite promising and encouraging for further work on the improvement of the proposed EDXRF identi-

Table 2. Values of N_{inc}/N_{coh} ratio and Z* as key parameters in the simple identification of unknown plastic materials

Sample		FTIR	NMR	N_{inc}/N_{coh}	Z*	XRF
Light	1	PS	PF	12.2	8.77	SBS, PF
Hair dryer	2	PS, ABS	PS, SBS	12.8	8.61	PF, SBS
Souvenir-key	3	PS	PS	13.4	8.46	PF, SBS
Soap box	4	PE	PE	36.4	5.73	PE
Pumice	5	PE	PE	29.7	6.21	PP
Yellow box	6	PP	PP	29.6	6.22	PP
Baby doll's head	7	PVC	PVC	8.3	10.2	PVC
Baby doll's body	8	PE	PE	35.9	5.77	PE
Swimming goggles	9	PVC	PVC	8.77	9.98	PVC
Souvenir thermometer	10	PS	PS	26.8	6.46	PA
Kinder egg	11	PP	PP	30.3	5.82	PP

* acrylonitrile butadiene styrene (ABS)

fication model. The different plastic additives to the main compound, and mixtures of various plastics in the artifact influence the index of incoherent/coherent scattering and should be further investigated. The calibration set of plastics suitable for conservation work should be limited and focused on types of widespread plastics such as cellulose nitrate (CN), cellulose acetate (CA), rubber, poly-urethane (PU), PVC and PA

The proposed EDXRF nondestructive model was found to be, fast, cheap, and offering also easy interpretation of the type of more or less pure plastics, and of additives. It can be also in the certain degree applied in the identification of type of plastics in artifacts from museum collections. It is also more than suitable for industrial use in quality control of plastics. In the case of a complex plastic matrix such as a mixture of various plastic compounds, the proposed identification model was of limited application. It would be very interesting to compare our non-destructive EDXRF approach with determination of elemental content and identification of plastics with alternative non-destructive analytical techniques like near IR spectroscopy (NIR) or terahertz, which are widely used in conservation area.

4. Conclusions

Validation of the proposed non-destructive EDXRF technique by the comparison with FTIR and NMR for the identification of unknown plastic types confirms that this new analytical approach was quite appropriate but also useful. It is cheap, fast, simple, and efficient in the identification of simple plastic matrices and their additives. Since its non-destructive nature it could be also a valuable analytical tool in the field of preservation of cultural heritage of plastic artifacts, a relatively new area, but with certain improvements. The identification model could be useful for the in-situ analysis of plastic objects in industry, waste management, and in other areas using the presently popular handheld EDXRF spectrometers.

5. Acknowledgements

The authors thank the Slovenian Research Agency for financial support within the framework of the research program P6-0282 “The object as representation, taste, reputation and strength (Investigation of material culture in Slovenia)”.

6. References

1. M. Nečemer, P. Kump, M. Žvanut, *X-ray Spectrom.* **2012**, *41*, 87–92.
2. G. Scott, Polymers in modern life. Polymers and the environment. Cambridge UK. The Royal Society of Chemistry, **1999**.
3. http://www.plastiquarian.com/index.php?id=7&subid=127.
4. T. Gruendling, S. Weidner, J. Falkenhagen,C. Barner-Kowollik, *Polym. Chem.* **2010,** *1,* 599–617.
5. G. Montaudo, F. Samperi, M. S. Montaudo, *Prog. Polym. Sci.* **2006,** *31*, 277–357.
6. L. M. Bodecchi, M. Cocchi, M. Malagoli, M. Manfredini, A. Marchetti*, Anal. Chim. Acta* **2005**, *554*, 207–217.
7. Y. R. Shashoua, *Polym. Degrad. Stabil.* **2003**, *81*, 29–36.
8. J. M. Chalmers, N. J. Everall, M. D.Schaeberele, I. W. Levin, E. N. Lewis, L. H. Kidder, J. Wilson, R. Crocombe, *Vibr. Spectrosc*. **2002***, 30*, 43–52 .
9. S. Bai, W. Wang, C. Dybowski, *Anal. Chem.* **2010***, 82,* 4917–4924.
10. B. Blümich, F. Casanova, J. Perlo, S. Anferova, V. Anferov, K. Kremer, N. Goga, K. Kupferschläger, M. Adams, *Acc. Chem. Res*. **2010**, *43*, 761–770.
11. L. Sereda , R. C. R. Nunes, M. I. B. Tavares, L. L. Y. Visconte, *Polym. Test.* **2002**, *21* 171–175.
12. R. W. Berg, A. D. Otero, *Vibrat. Spectrosc.* **2006***, 42*, 222–225.
13. J. M. Chalmers, N. J. Everall, *Trends Anal. Chem*. **1996**, *15*, 18–25.
14. F. Vanhaecke, M. Resano, L. Moens, *Anal. Bioanal. Chem.* **2002**, *374*, 188–195.
15. A. Ritter, E. Michel, M. Schmid, S. Affolter, *Polym. Test.* **2004**, *23*, 467–474.
16. J. V. G. Adelantado, V. P. Martinez, F. B. Reig, M. T. D. Carbo, F. B. Mossi, *Anal. Chim. Acta* **1993***, 276*, 39–45.

17 K. Nakano, T. Nakamura, *X-ray Spectrom*. **2003**, *32*, 452–457.

18. P. Kump, M. Nečemer, B. Smodiš, R. Jačimovič, *Appl. Spectrosc*. **1996**, *50*, 1373–1377.
19. K. M. Bichinho, G. P. Pires, F. C. Stedile, *Spectrochim. Acta Part B* **2005**, B60, 599–604.
20. C. Vázquez, S. Boeykens, H. Bonadeo, *Talanta* **2002**, *57*, 1113–1117.
21. S. Boeykens, C. Vázquez, *Spectrochim. Acta Part B* **2004**, B59, 1189–1192.
22. M. A. Bellara, J. M. Anzano, J. R. Castillo, *Analyst* **1990**, *115*, 955–957.
23. Q. Godoi, D. Santos Jr, L. C. Nunes, F. O. Leme, I. A. Rufini, J. A. M. Agnelli, L. C. Trevizan, F. J. Krug, *Spectrochim. Acta Part B* **2009***,* B64, 573–581.
24. J. Grdadolnik, *Acta Chim. Slov.* **2003**, *50*, 777–788.
25. E. O. Stejskal, J. Schaefer, M. D. Sefcik, R. A. McKay, *Macromolecules* **1981**, *14*, 275–279.

Povzetek

Intenziven razvoj in velika proizvodnja plastičnih materialov v preteklem stoletju se med drugim kaže tudi v povečanem številu plastičnih predmetov v muzejskih zbirkah. Razvoj enostavne in hitre tehnike za določitev vrste plastik bi lahko uporabili pri pakiranju hrane, sortiranju odpadnih plastik pa tudi pri muzejskem konzervatorskem delu na plastičnih eksponatih v muzejskih zbirkah, predvsem ker je metoda nedestruktivna. V našem prejšnjem prispevku smo predstavili nedestruktivno metodo energijsko disperzivne rentgenske fluorescenčne spektrometrije[1] za hitro identifikacijo vrste plastik, ki smo jih prav zaradi nedestruktivnosti metode raziskovali na nekaj plastičnih predmetih iz muzeja. Za validacijo naše tehnike je nujno da uporabimo za ta namen primerjavo s tehnikami kot so Fourierjeva infrardeča spektroskopija in Nuklearna magnetna resonanca, izbranih izmed mnogih drugih uveljavljenih tehnik, ki se zalo veliko uporabljajo za identifikacijo plastik. V tem prispevku želimo z validacijo EDXRF tehnike za nedestruktivno identifikacijo nekaterih običajnih vrst plastik pokazati na splošno uporabnost te tehnike na različnih področjih uporabe plastičnih materialov.