Nurbanu Yanar

Institute of Raw Material Preparation and Environmental Processing,
University of Miskolc, Hungary

LAB-SCALE INVESTIGATION OF RAMAN SPECTROSCOPY FOR PLASTICS RECYCLING

ABSTRACT

Our society is now faced with the environmental and sustainability problems of the extensive usage of different plastic made goods and products. Raman spectrometry is a suitable option for waste plastic particles identification. Systematic tests have been carried out with a handheld Raman device for the identification of differently loaded plastic particles. Some real waste samples and mono-material plastic model pieces have been selected. These were polyamide (PA), polycarbonate (PC), polypropylene (PP), polyethylene terephthalate (PET) and, light and dark-coloured acrylonitrile butadiene styrene (ABS), and polyvinyl chloride (PVC). A turning machine, a hammer mill and a cutting mill were used to load the samples before the identification. Raman spectra were detected and the so called feature: "matching percentage" was determined. Conclusions about the usability issues of the device have been drawn.

INTRODUCTION

Plastics are indispensable part of our lives. We have been using plastics since 1950. The amounts of plastics consumed have grown since then, because of its beneficial properties such as strength, fabrication capabilities, durability, low weight, low density, low-cost, etc. (Subramanian, 2000). The identification and classification of plastics play a critical role in waste management and recycling processes. Sorting of plastics into categories is important due to the various characteristics that each resin types hold. Identification and classification methods of plastic wastes range from manual sorting to advanced automated technologies. The techniques are usually based on chemical, optical, electrical, or physical property differences between plastics such as different melting behaviour, rheology, and thermal stability (Scheirs, 1998). For example, some components may be melted while others remain solid in case of thermal processing (Scott, 1995). Automated sensor-based sorting is an established technology with applications in various processing operations. Automated waste sorting is expensive and not as common as manual sorting at the moment in developing countries. There are numerous automated sorting techniques for recovering various recyclable waste fractions such as metal, plastic, paper, glass, and wood. Direct sorting and indirect sorting are the two types of automated waste sorting techniques. Direct sorting techniques utilize material properties such as magnetic susceptibility, electrical conductivity, and density for heavy media separation by applying external fields like magnetic, eddy current, and gravity respectively (Gaustad et al., 2012; Mesina et al., 2003; Svoboda, 2004; Faitli et al., 2018; Faitli et al., 2019a and 2019b). On the other hand, indirect sorting applies sensors to detect the presence and the location of recyclables in the waste so that automated machines or robots can be employed to sort the detected recyclable materials (Gundupalli et al., 2017). Spectroscopy-based sorting is a subcategory of indirect automated sorting. The plastic waste sample is enlightened in spectroscopy-based techniques. The interaction between light and the sample is a unique set of wavelengths as the light gets reflected differently for each type of plastic

existing in the sample. There are various spectroscopy methods such as: infrared spectroscopy, mid-infrared spectroscopy, near-infrared spectroscopy, fourier-transform infrared spectroscopy, X-ray spectroscopy and, Raman spectroscopy. Sensors are used for reading the signature of reflected wavelengths from the target material. Afterwards, the material to be sorted out is determined by the processor unit (Gundupalli, et. al. 2017).

Operating Principles of Raman Spectroscopy

When a sample is exposed to monochromatic light in a visible region, the sample absorbs light and, the major portion of the light gets transmitted through the sample. However, a minor part of the light is scattered by the sample in all the directions. One can observe the scattering at the right angle to the incident beam. The incident light has a particular frequency. If the scattered light has the frequency same as the incident light, then scattering is called Rayleigh scattering. However, it has been observed that about 1% of the total scattered intensity occurs at frequencies different from the incident frequency. This is called as Raman scattering. Raman scat can be thought of as a two-photon process. The electrons have different vibrational levels. They are defined by specific energy differences. When an incident monochromatic light interacts with an electron in the sample, the electron absorbs energy from the incident photon and it rises to a virtual state of energy. The energy transform is given by the formula $E=hv$ where v is the frequency of the incident photon. The electron falls back to an energy level by losing energy. If the energy loss equals the energy of the incident photon, the electron falls back to its initial level and in this process emits another photon. Since the energy loss is equivalent to the energy of incident photon then released photon has the same frequency as the incident photon. As the frequency is the same, Rayleigh scattering occurs. However, sometimes electrons when losing energy from the virtual state, can fall back to a different vibrational level, in this case, the energy loss by the electron is different than the energy absorbed from the incident photon. As a result, the photon emitted by the electron has energy different than the incident photon. This is possible when the frequency of the emitted photon is different than the incident photon. This gives rise to Raman scattering. Depending on the final energy of the electron or final vibrational level of the electron, Raman scattering can be separated into Stokes scattering and Anti-Stokes scattering. If the frequency of the scattered photon is less than the incident photon, Stokes scattering is observed on Raman spectrum. This happens when the electron absorbs energy. Similarly, when the frequency of the emitted photon is greater than the incident photon, Anti-Stokes scattering is observed. This means that energy is released by the electron. By studying the spectra, one can identify the rotational levels and thus a particular molecule. Similarly, the intensity value of a particular Raman scattering helps to determine the concentration of a molecule in a sample. In this matter, quantitative analysis can be done. In all three types of scattering, an incident photon of energy hv raises the molecule from a vibrational state to one of the infinite numbers of virtual states located between the ground and the first electronic state. The type of scattering observed is dependent on how the molecule relaxes after excitation. Rayleigh scattering is by far the most common transition, due to the fact that no change has to occur in the vibrational state of the molecule. The anti-Stokes transition is the least common, as it requires the molecule to be vibrationally excited before the photon is incident upon it.

MATERIALS AND METHOD

Polymers are large, complex molecules, yet their spectra may be relatively simple. Six different kinds of plastics were collected for laboratory measurements. All of the samples were flat. The samples were not cleaned before measurements, and in some cases, they were

© Yanar N: Inst. of Raw Material Prep. and Environmental Proc., University of Miskolc

notably dusty on their surfaces. The measurements of the black and grey coloured samples were not successful due to their colour, as a result of the absorption of the laser light by dark colours. Fig. 1 shows the model material samples.
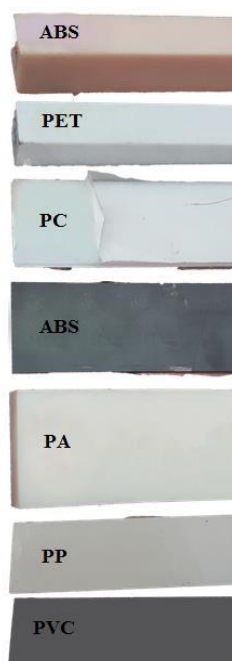
Samples were;
- Polyamide (PA),
- Polycarbonate (PC),
- Polypropylene (PP),
- Polyethylene terephthalate (PET)
- Polyvinyl chloride (PVC) and,
- Acrylonitrile butadiene styrene (ABS).

Figure 1. Original Model Plastic Samples

Raman measurements were performed using a handheld Raman spectrometer, Progeny TM (Rigaku Raman Technologies, Wilmington, DE, USA), equipped with a 1064-nm CLASS 3b laser which emits beam between 30 - 490 milliwatts. Class 3b lasers are hazardous for eye exposure. They can heat skin and materials but are not considered a burn hazard.

Laser Beam Properties:

Properties: **Progeny 1064**
Power: **30-490 mW (Progeny LT 300mW max)**
Frequency: **1064 nm**
Lens focal length: **11 mm**
Focused spot diameter: **25 microns**

Figure 2. Handheld Raman Spectrometer

The Raman spectrometer was factory calibrated for wavenumber accuracy according to ASTM E1840-96 using benzonitrile and verified with cyclohexane and naphthalene. It has a user-selected calibration module based on a certified benzonitrile calibration standard. The

Instrument Calibration was run using a certified calibration sample standard (Benzonitrile) provided by the company to ensure that the instrument accurately collects and processes spectral data and resets its Certification Status. The benzonitrile standard was placed into the sample holder for the best result. The spectrometer passed the calibration test. To ensure the result, the Performance Verification test was performed and passed too.

Figure 3. Samples after the turning machine process

Mechanical processing, namely loading of the samples were carried out in a turning machine, a hammer mill and a cutting mill. A standard 3 kW power turning machine with vertical cutting tool shaft was used. A standard 4 kW hammer mill made by the Institute of Raw Material Preparation and Environmental Processing with four hammers and 10 mm openings size underneath screen was used. A 2.2 kW power, 1500 rpm rotor revolution and 129.5 mm cutting disc diameter Retsch cutting mill was also used.

RESULTS AND DISCUSSION

Figure 3 shows the plastic chips produced by the turning machine.

Figure 4 shows samples which were used for the hammer mill experiment.
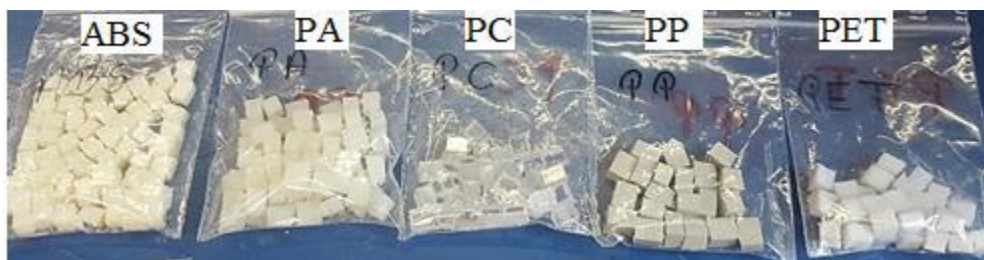

Figure 4. Samples which were used for the hammer mill experiment

The results of the measurements before and after the mechanical loading of the samples are as follows. Both measurements of the original samples and of the loaded samples have different codes. Settings were updated for each sample to be able to get the best spectrums. Codes and settings can be seen in Table 1. Figure 5 shows the measures spectra of tests PA.0 and PA.1 for comparison. Figure 6 compares the results of the PC.0 and PC.1 tests, while Figure 7 shows the measured spectra of the PP.0 and PP.1 tests.

Table 1

Specifications of each measurement

| Sample and test identifier	Used Machinery	Code	MW	Msec	Averages
ABS/black	-	ABS.b.0	70	1500	5
ABS/black	Turning Machine	ABS.b.1	NA	NA	NA
ABS/black	Cutting Mill	ABS.b.2	35	2500	10
ABS/cream	-	ABS.c.0	490	3000	10
ABS/cream	Turning Machine	ABS.c.1	490	3000	10
ABS/cream	Hammer Mill	ABS.c.2	275	4500	10
PET	-	PET.0	490	1500	10
PET	Turning Machine	PET.1	490	1500	10
PET	Cutting Mill	PET.2	490	1500	10
PC	-	PC.0	490	1500	10
PC	Turning Machine	PC.1	490	1500	10
PC	Hammer mill	PC.2	100	4500	10
PC	Cutting Mill	PC.3	490	4500	2
PA	-	PA.0	490	3000	10
PA	Turning Machine	PA.1	490	3000	10
PA	Cutting Mill	PA.2	490	3000	10
PP	-	PP.0	300	3000	10
PP	Turning Machine	PP.1	300	3000	10
PP	Cutting Mill	PP.2	300	3000	10
PVC	-	PVC.0	NA	NA	NA
PVC	Turning Machine	PVC.1	55	2500	10
PVC	Cutting Mill	PVC.2	55	2500	10
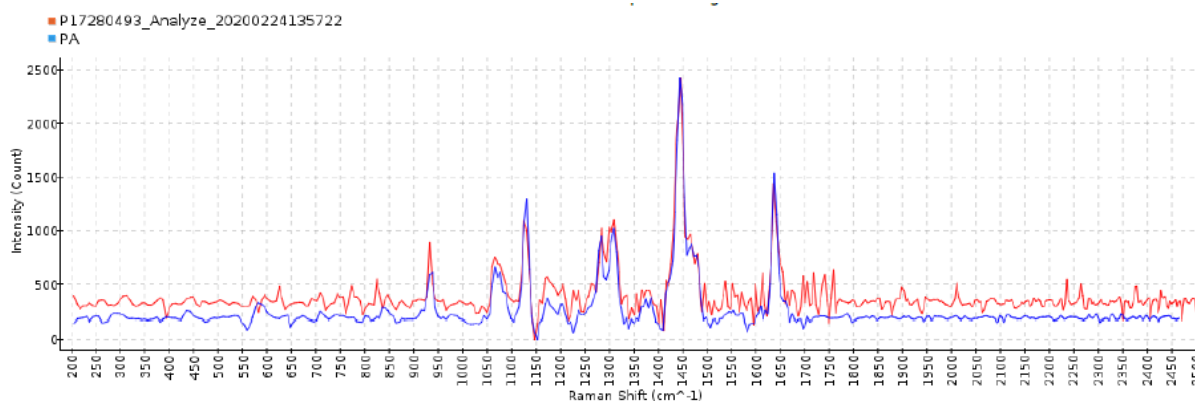
Figure 5. Comparison of PA.0 and PA.1
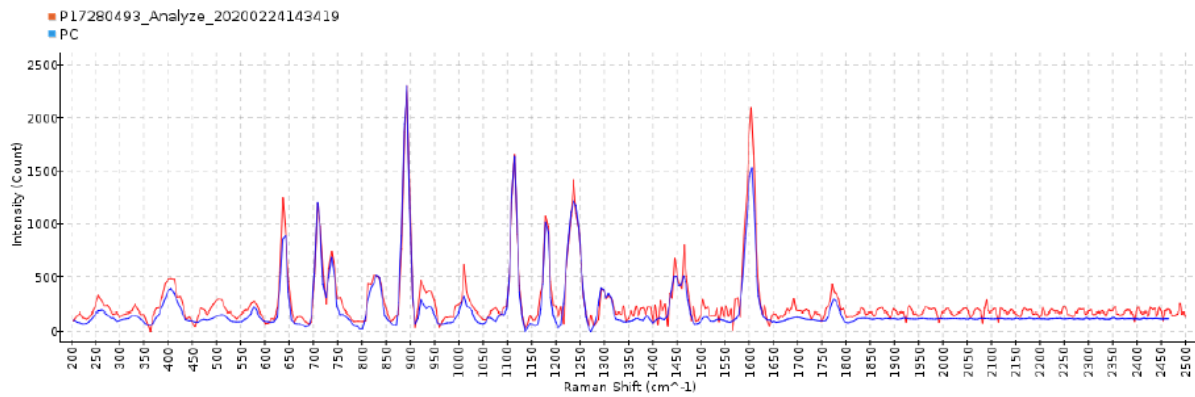
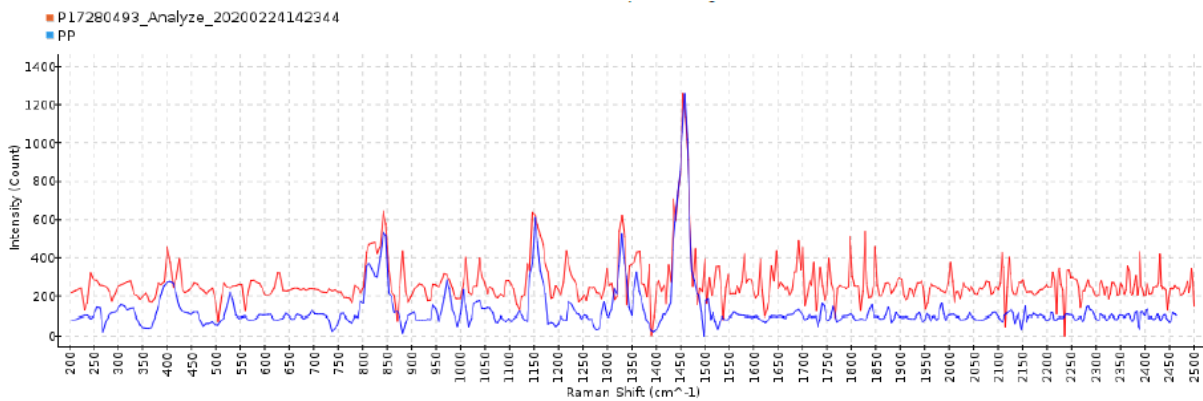*Figure 6. Comparison of PC.0 and PC.1*

Figure 7. Comparison of PP.0 and PP.1

Measurements of the Hammer Mill Process

Hammer mill can be used as a crusher for brittle materials. Since the polymers are elastic and not brittle materials, the cubic samples were only rounded on the edges, and they were burnt due to the heat that was produced by the hammer mill's rotation. Figure 8 shows the rounded ABS and PC particles after the hammer mill loading.
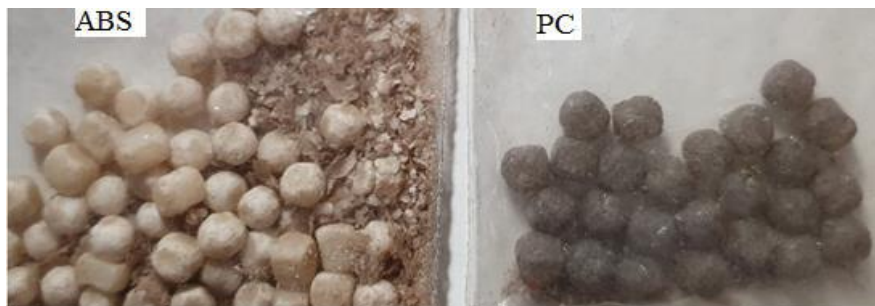

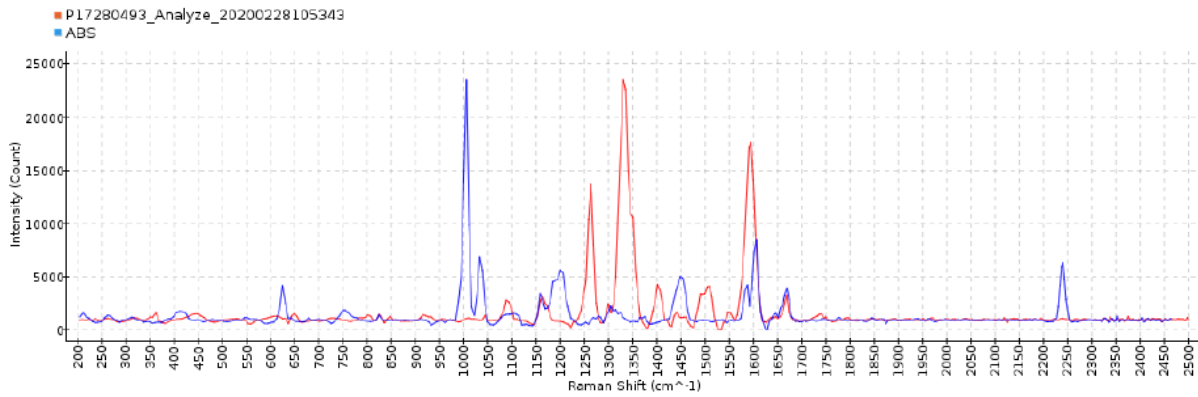*Figure 8. Results of the hammer mill experiment*

Figure 9. Comparison of ABS.c.0 and ABS.c.2

Measurement of the Cutting Mill Process

The obtained comminution ratio of the PET was better than the other samples. In addition to this, the comparison of the original PET sample and the loaded sample shows a 99% match percentage. Figure 10 shows the samples of the PVC.1 and PVC.2 tests.
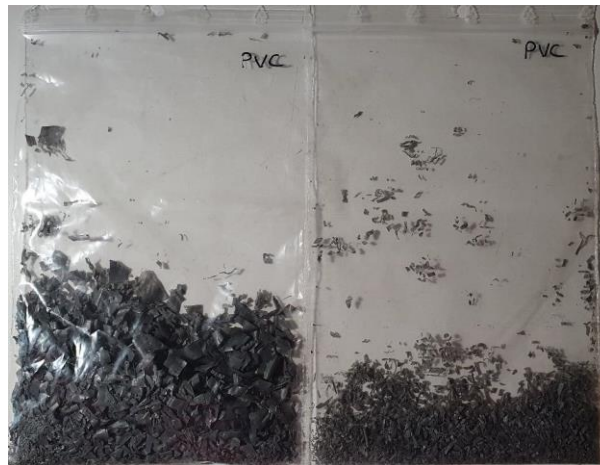

Figure 10. PVC.1 and PVC.2

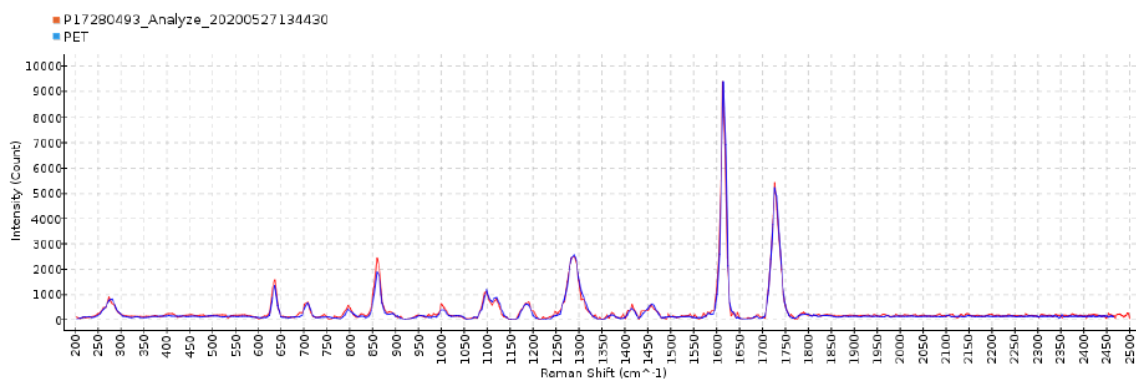Figure 11 shows the measured spectra of PET.0 and PET.2 tests.

Figure 11. Comparison of PET.0 and PET.2

© Yanar N: Inst. of Raw Material Prep. and Environmental Proc., University of Miskolc

7

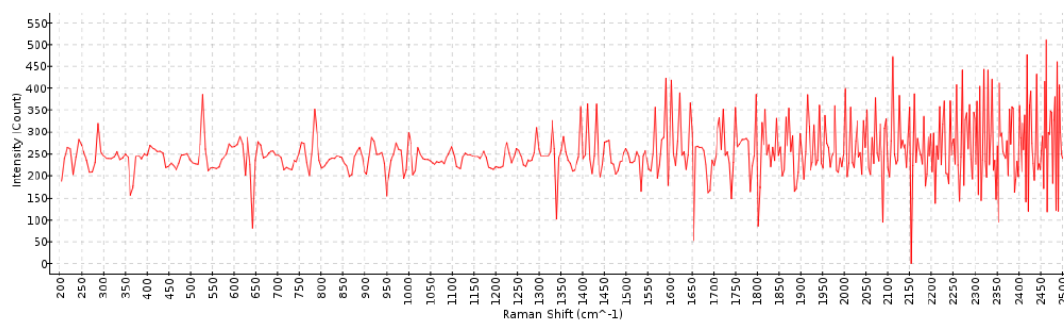Figure 12 shows the measured spectrum of the PVC.2 test.

Figure 12. PVC.2

ABS and PVC measurements weren't successful due to the noise. As Figure 12 indicates, signals of dark samples, black and grey, were very low in intensity and no polymer specific peak could be observed. This is a common phenomenon found in many spectroscopic techniques and is due to the absorption of the laser light by dark colours.

CONCLUSION

This study shows that the Raman spectrophotometer can be used to identify numerous polymers of different colours by measuring their spectra and matching them with a library. The identification takes just a few seconds. Problems occur only when dark-coloured polymers have to be analysed. Such samples strongly absorb the spectrometer's laser light and thus, some polymer-specific peaks don't appear in the spectrum. Dark-coloured samples, therefore, cannot be identified by Raman spectroscopy.

Theoretically, the Raman bands should become broader as particle size gets smaller and it should decrease in intensity. Though, only the decrease in intensity was observed in this study. Raman spectroscopy is less sensitive to particle size than NIR. Regarding the recycling applicability of the used mechanical loading processes, the turning machine is not an option because it is used in machine production. The cutting mill is the best option for plastic wastes preparation since it has the capability to liberate any kind of polymer.

In respect to polymers used in this study, the best identification results were obtained with the PET sample, regarding the comminution ratio as well as the match of the original sample and the sample after the cutting process. For these reasons, Raman spectroscopy can be a second option to NIR and it can be used in terms of waste analysis and then recycling of PETs.

ACKNOWLEDGEMENT

REFERENCES

[1.] **V. Allen, J.H. Kalivas, R.G. Rodriguez**: Post-consumer plastic identification using Raman spectroscopy, Appl. Spectrosc. 53 pp. 672–681. (1999)
[2.] **Buschow, K.J., Cahn, R.W., Flemings, M.C., Ilschner, B., Kramer, E.J. and Mahajan, S.:** Encyclopedia of materials. Science and technology, 1, p.11. (2001)

© Yanar N: Inst. of Raw Material Prep. and Environmental Proc., University of Miskolc

[3.] **Dalm, M., Buxton, M.W., van Ruitenbeek, F.J. and Voncken, J.H.**: Application of near-infrared spectroscopy to sensor-based sorting of a porphyry copper ore. Minerals Engineering, 58, pp.7-16. (2014)

[4.] **J, Faitli; B, Csőke; R, Romenda; Z, Nagy; S, Németh:** Developing the combined magnetic, electric and air flow (KLME) separator for RMSW processing. WASTE MANAGEMENT & RESEARCH 36 pp. 779-787. (2018)

[5.] **Faitli, J; Nagy, S; Romenda, R; Gombkötő, I; Bokányi, L; Barna, L.:** Assessment of a residual municipal solid waste landfill for prospective 'landfill mining' WASTE MANAGEMENT & RESEARCH 29 Oct. p. 11 (2019a)

[6.] **Faitli, J.; Romenda, R.:** Detailed Sampling Protocol for the Analysis of Residual Municipal Solid Wastes. In: K., Moustakas; M., Loizidou (eds.) Proceedings of the 7th International Conference on Sustainable Solid Waste Management Herakleion, Görögország: Hellenic Mediterranean University, Paper: Session XXIII. paper 10., 10 p (2019b)

[7.] **Gaustad, G., Olivetti, E., Kirchain, R.:** Improving aluminium recycling: a survey of sorting and impurity removal technologies. Resour. Conserv. Recycl. 58, pp. 79–87. (2012)

[8.] **Gundupalli, S.P., Hait, S. and Thakur, A.:** A review on automated sorting of source-separated municipal solid waste for recycling. Waste management, 60, pp.56-74. (2017)

[9.] **Hopewell, J., Dvorak, R. and Kosior, E.:** Plastics recycling: challenges and opportunities. Philosophical Transactions of the Royal Society B: Biological Sciences, 364(1526), pp. 2115-2126. (2009)

[10.] **Mesina, Catalina T., et al.** "Effects of attenuation correction and reconstruction method on PET activation studies." Neuroimage 20.2 pp. 898-908. (2003)

[11.] **Niaounakis, M.:** Biopolymers: Reuse, Recycling, and Disposal. William Andrew. chapter 5. Physical Recycling. Plastics Design Library, pp. 1151–163. (2013)

[12.] **Rutkowski, Joseph V., and Barbara C. Levin.** "Acrylonitrile–butadiene–styrene copolymers (ABS): Pyrolysis and combustion products and their toxicity—a review of the literature." Fire and materials 10.3-4 pp. 93-105. (1986)

[13.] **Safavi, S.M., Masoumi, H., Mirian, S.S., Tabrizchi, M.,** "Sorting of polypropylene resins by colour in MSW using visible reflectance spectroscopy" Waste Management 30, pp. 2216-2222. (2010)

[14.] **Scott, D. M.:** A Two-Colour Near-Infrared Sensor for Sorting Recycled Plastic Waste. Measurement Science and Technology, v6 n2, February, 156-159. (1995)

[15.] **Scheirs, J.:** Polymer Recycling, Wiley Publication, (1998)

[16.] **Scott, D. M.:** A Two-Colour Near-Infrared Sensor for Sorting Recycled Plastic Waste. Measurement Science and Technology, v6 n2, February, 156-159. (1995)

[17.] **Svoboda, J.:** Magnetic Techniques for the Treatment of Materials. Springer. (2004)

[18.] **P. M. Subramanian,** "Plastics recycling and waste management in the US," Resour. Conserv. Recycl. 28, 253–263. (2000)