Eighth World Conference on Sampling and Blending

Paper Number: 85

Plastics Recycling and Sampling

H J Glass[1] and S C Dominy[2,3]

1. Rio Tinto Professor of Mining and Minerals Engineering, Camborne School of Mines, University of Exeter, Penryn, Cornwall TR10 9FE, UK. Email: h.j.glass@exeter.ac.uk
2. FAusIMM(CP), Visiting Associate Professor, Camborne School of Mines, University of Exeter, Penryn, Cornwall TR10 9FE, UK. Email: s.dominy@e3geomet.com
3. Adjunct Professor, Department of Mining and Metallurgical Engineering, Western Australian School of Mines, Curtin University, Bentley, WA 6102, Australia.

ABSTRACT

This contribution examines the effect of feedstock sampling before the sorting stage of PET bottle recycling. Batches of waste PET bottles may contain non-PET bottles which need to be removed by sorting. Any residual presence of PVC is detrimental for the quality of products manufactured from recycled PET. The maximum tolerated concentration of PVC in cleaned PET is extremely low, which places high demands on the recovery of PVC achieved by sorting. To be confident of attaining the desired PET quality after sorting, acceptance sampling of truckloads of PET bottles may take place prior to sorting. It is shown that accounting for sampling uncertainty requires that the sorting process achieves a consistently high recovery of PVC bottles.

INTRODUCTION

Plastic recycling

It has long been recognised that waste plastics constitute a valuable resource whose recycling can help preserve non-renewable oil resources and reduce carbon dioxide emissions. Back in 1988, the Society of the Plastics Industry introduced a plastics identification system which manufacturers could use to mark individual plastic products. A numerical code, surrounded by three chasing arrows, indicates the most common types of plastic (Figure 1). This design was intended to promote awareness of plastics recycling and enable plastic recycling companies to quickly identify the type of plastic in a sorting process. Plastics labelled 1 to 6 represent over 80 per cent of plastics used globally while other plastics are indicated with 7. The effectiveness of codes is subject to debate. For example, the codes do not match the ranking of plastics in terms of use: PolyPropylene (PP, label 5) and PolyVinylChloride (PVC, label 3) are used in larger quantities than PolyEthyleneTerephtalate (PET, label 1) (Plastics – the Facts 2016). The codes also do not indicate environmental friendliness of the plastic: residual monomer, intermediate reaction products, solvents, and additives may migrate from the plastic during use and lead to uptake by humans. It is difficult to quantify the risk plastics pose to human health, which often leads to confusion. For example, a building block of PolyCarbonate (PC, label 7) plastics, BisPhenol A (BPA) was introduced commercially in 1957 and has attracted much attention in recent years. BPA is suspected to be potentially harmful to the human endocrine system (vom Saal *et al*. 1998) and was banned from plastic baby bottles in the EU in 2011 (Commission directive 2011/8/EU). In 2015, France implemented a blanket ban on BPA in food contact materials (Constitutional Council Decision no. 2015-480). In the same year, however, a European Food Safety Authority report (EFSA, 2015) concluded that human exposure to BPA was well below a tolerable daily intake of 4 micrograms BPA per kilogramme of body weight. In the meantime, alternatives to BPA are emerging which, being chemically similar to a certain degree, may or may not produce estrogenic effects (Bittner, Yang and Stoner, 2014). If mixtures of different types of PC start to appear in recycling streams, will it be possible to identify and sort these to comply with regulatory requirements?

Plastic additives

Plastics may contain additives to improve functional properties such as plasticity, rigidity, resistance to oxidation, heat, cold and impact, clarity, colour, and flame retardancy. A plastic additive to attract scrutiny is PolyBrominated Diphenyl Ether (PBDE) which has found widespread application as a flame retardant. PDBE leached from plastics is persistent in the environment and is able to bioaccumulate (Rahman *et al*. 2001). The potential health effects of the family of PBDE compounds have been widely studied. In 2011, EFSA reported that pentaBDE (BDE-99) is the only PDBE congener for which current dietary exposure represents a health concern (EFSA, 2011). This raises the question whether it is possible to discriminate between waste plastics containing different forms of PBDE?

Single- versus multiple-use PET bottles

The recycling potential of waste plastics is influenced by the chemical structure, the presence of additives, the application history, and the sortability. Hence, plastic recycling cannot be based solely on sorting waste plastics according to the plastic code. Consider, for example, the development of recycling PolyEthylene Terephthalate (PET) bottles in the Netherlands and Germany. In the 1990s, deposit schemes were introduced to encourage consumers to return PET bottles to designated collection points. The collection of whole PET bottles enables these to be re-used after washing. The collection side of the scheme proved popular and return rates around 95 per cent are recorded (Stichting Rerourverpakking Nederland, 2016). Bottle cleaning and re-use revealed a number of issues: sorbed food components may be difficult to remove, residues of cleaning chemicals may linger, PET may start to degrade after multiple cycles of re-use, and damage to bottles may prevent further re-use (Widén, Leufvén and Nielsen, 2005). In view of these matters, single-use PET bottles, which are made with a lower concentration of copolymers, continue to be popular with the plastics industry and are subject to a more conventional recycling process. A typical recycling flowsheet for single-use PET bottles (Figure 2) starts with collection of bottles from consumers and separating out non-PET bottles by recycling companies. Bales of PET bottles are then transported to manufacturing companies which crush the plastic into a flaky product called granulate. The granulate may be upgraded through a wet sink-float process to separate non-PET flakes, for example caps made of PP or HDPE, and washed to remove residual contaminants such as labels. The cleaned granulate is dried, extruded and shaped into bottles through blow moulding (Hopewell, Dvorak and Kosior, 2009; Welle, 2011).

PLASTIC SORTING

Characterisation with near infrared sensors

Products made from recycled plastic need to meet stringent quality standards, which places emphasis on control of the stages of the recycling process. During the initial sorting stage, for example, modern recycling processes make extensive use of sensors for rapid, real-time analysis. Plastics are particularly amenable to rapid characterisation by interpretation of measurement of the reflectance from a plastic surface illuminated with near infrared light. Near infrared refers to a range of electromagnetic wavelengths (700-2500 nm) which borders on the visible light spectrum (400-700 nm). Some chemical bonds present in plastics, such as those between carbon, hydrogen and oxygen, are capable of absorbing specific wavelengths of infrared light, reducing the reflectance and creating absorption features. Differences in plastic composition lead to the presence or absence of features, or to shifts in wavelengths where features display maximum absorption of infrared light. Near infrared sensors allow monitoring of the real-time composition of plastics during processing. This information can also be used to sort plastics according to type (Scott, 1995). By keeping track of plastic pieces after measurement, a downstream sorting process can be triggered if required. Separation of target bottles is achieved by ejecting these with an array of air jets. In an industrial setting, pieces of plastic are processed at high speed, passing through a sensor-based sorting system at about 3 meters per second. Sensor-based sorting has evolved to become competitive with the traditional process of manual sorting.

PET bottle recycling and PVC

In the following, PET bottle recycling is discussed in terms of sensor-based sorting and the role of sampling on required sorting performance. Incidental misclassification of PET bottles during sorting may occur, for example when measurement of lids and labels cause a PET bottle to be identified as a non-PET bottle, or when a non-PET bottle is inadvertently sorted as a PET bottle due to close proximity to PET bottles (Tachwali, Al-Assaf and Al-Ali, 2007). The separation efficiency states that the recovery of PET bottles in a product fraction is reduced through the accidental co-recovery of non-PET bottles. The latter is relevant when the residual presence of non-PET plastic has a detrimental effect on the quality of products made from recycled PET. A notorious example is PVC, which is in circulation in some countries as bottles similar in shape and size to PET bottles. As a consequence, PVC and PET bottles may end up in the same waste stream. PVC is unstable at temperatures where PET is moulded (270°C), and degrades through the evolution of hydrochloric acid. This will produce discoloration of PET flakes and black specks on freshly extruded PET bottles

(Awaja and Dumitru, 2005). PET recycling requires that the concentration of PVC flakes in PET granulate is at levels where the effect of PVC is negligible. In practice, the maximum tolerated concentration of PVC flakes in PET granulate is set at 50 ppm (parts-per-million) (Pawlak *et al*. 2000). Separating PVC flakes with a sink-float process is not feasible in view of the relatively small difference in density between PET (1.38 g/cm^3) and PVC (1.45 g/cm^3). A sensible option is to avoid formation of PVC flakes by removing PVC bottles at an earlier stage of recycling, through selective collection and sensor-based or manual sorting.

PLASTIC SAMPLING

Acceptance sampling

The collection of spent PET bottles is frequently performed by specialised companies who supply recycling companies with feedstock for sorting. If the sorting company has concerns about the composition of a lot or batch, which consists of a truckload of bottles, acceptance sampling is performed (Figure 3). Inspection of a truckload containing around 14 t is based on analysis of a sample consisting of two randomly-selected bales weighing about 200 kg each. The first sample bale is analysed and, if its quality is deemed to be insufficient, an assessment is made whether analysis of the second bale could lead to a verdict of sufficient quality from combined analysis of both bales. Note that if there is no prospect of observing sufficient quality from analysis of both sample bales, analysis of the second bale is forfeited (Texplast GmbH, *pers. comm.*).

The total sample size represents about three per cent of the truckload, which is a considered to be a manageable sample size. Given a degree of selectivity in the collection process, the mass of PVC found in the sample is normally attributable to a relatively small number of PVC bottles. Hence, the presence of PVC will be expressed in terms of the number of PVC bottles. The PVC mass may be converted into the number of PVC bottles and vice versa through the observed average mass of a PVC bottle, which is roughly 40 g. In a sample of 400 kg, a PVC bottle of 40 g contributes 100 ppm to the sample PVC concentration. This is twice the maximum tolerated concentration of PVC in a batch of PET after cleaning. Clearly, a highly efficient sorting process is required to separate out PVC bottles. If the sorting process is expected to recover 90 % of the PVC bottles, a sample of 400 kg could contain 5 PVC bottles and, provided that the sample is representative, the batch of PET should meet the tolerated level of PVC after cleaning (equal to 0.5 bottle of PVC per unit sample).

The mass of PVC will only constitute a small fraction of the total mass of a sample and, by implication, the batch. In that case, the percentage of PVC bottles which sorting is expected to recover from the batch follows from:

$$\text{PVC recovery (\%)} \simeq 100\left(1-\frac{x_{\text{product}}}{x_{\text{feed}}}\right) = 100\left(1-\frac{50}{100\text{N}}\right) = 100\left(1-\frac{1}{2\text{N}}\right) \qquad (1)$$

where x_{feed} is the initial PVC concentration before sorting, $x_{product}$ is the maximum tolerated PVC concentration after sorting, and N is the number of PVC bottles found in the sample. Although Equation (1) assumes that the sample is representative for the batch, there is no guarantee this is true unless the entire batch were sampled. The repeated drawing, analysis, and replacement of equisized samples from the same batch would reveal varying numbers of PVC bottles in individual samples. In the absence of systematic bias, classification of the number of PVC bottles in these samples would show a sampling distribution which is centred on a representative number of bottles in the sample. The width of the sampling distribution is influenced by sample size which, when accounted for properly, may affect the PVC recovery to be delivered by sorting.

Interpretation of sample analysis

Inspection sampling of a truckload of PET bottles is based on analysis of a single sample following an established statistical procedure. The result of the sample analysis represents an arbitrary point on the sampling distribution and should not be compared directly to the maximum tolerated PVC concentration in a sample. Instead, a decision to accept or reject a batch of PET bottles is based on comparison of the observed number of PVC bottles in a sample with some critical threshold. This threshold is determined by calculating a value for the sampling uncertainty and subtracting this value from the maximum tolerated PVC concentration, i.e. 50 ppm PVC. Analysing a sample which forms a small portion of the batch leads to a more stringent requirement with respect to the maximum concentration of PVC found in the sample. Note that sampling uncertainty takes into account the sample size, expressed in terms of the number of PET and PVC bottles, the proportion of PVC bottles, and the reliability of making the correct decision regarding the quality of the batch.

Defining a critical threshold for interpretation of the sample analysis result assumes that a sample contains the critical threshold concentration of PVC from sampling a batch which contains exactly the maximum tolerated PVC concentration. There is a statistical element to this approach: the highest probability, P, of encountering a sample analysis result which is below the threshold concentration but from a batch where the PVC concentration is equal to the maximum tolerated concentration is determined by a chosen level of significance of a statistical test regarding the quality of the batch. In equation:

$$P(x_{sample} < x_{critical} \mid x_{batch} = x_{product}) = 1 - \alpha \quad (2)$$

where α is the level of significance of the test (between 0 and 1). Note that the complement of the level of significance is the reliability of making the correct decision with regards to the batch. The test is implemented through the following steps:

i) a sampling distribution is constructed about the maximum tolerated PVC concentration using a calculated sample standard deviation;
ii) a reliability is selected based on economic considerations;
iii) a critical threshold is defined by introducing the sampling uncertainty; and
iv) a decision about the quality of the batch is reached by comparing the sample analysis result with the critical threshold.

If the sample contains less PVC than the critical threshold, the batch is accepted on the basis that the correct decision is being made in accordance with the specified reliability. If it later emerges that there was more PVC in the batch than the maximum tolerated level, this would be attributable to a small but feasible probability of drawing a sample with less PVC than the critical threshold from that batch. As illustrated in Figure 4, this would be denoted a type I error, also known as the consumer’s risk. Figure 4 also shows that the probability of a Type II error can be substantial if the quality of the batch is close to the maximum tolerated level of PVC.

Sorting recovery

A reverse procedure to sample analysis interpretation is used to determine the required recovery of PVC bottles with a sorting process. Starting point is the assumption that, due to sampling uncertainty, the number of PVC bottles in a feed sample will be less than the expected number of PVC bottles in a sample. Taking into account the sampling distribution about the expected number of bottles in a representative sample from the batch and the reliability of making the correct decision about accepting the batch for sorting, the expected number of PVC bottles in the sample is discerned. It is notable that the shape of the sampling distribution is approximately Gaussian if the sample size is not too small and the property of interest is not too rare. With PET recycling, the number of PVC bottles in a sample of 400 kg is likely to be small, say less than eight. For this low number of PVC bottles, the sampling distribution displays a pronounced tail towards higher numbers of PVC bottles and is adequately described by a discrete Poisson distribution. The shape of the Poisson distribution is governed by a single parameter, λ, which is equal to both the modal average and the variance of the distribution. As shown in Figure 5, the Poisson distribution approximates the Gaussian distribution as the number of bottles increases, albeit for the case where the average equals the variance. It should be noted that the choice of reliability will be applied in an approximate manner because the Poisson distribution specifies the probability associated with discrete numbers of bottles.

In a batch of 14 t of waste PET, 50 ppm of PVC equates to – on average – 17 to 18 bottles of PVC in the batch. This translates – on average - to 0.5 a PVC bottle in a representative 400 kg sample of cleaned PET. While any PVC bottle found in a 400 kg sample drawn from the cleaned PET is too much, sampling batches of PET after cleaning is not meaningful. Acceptance sampling of PET feedstock to the sorting process may be useful if recovery of PVC by the sorting process is understood. Figure 6 shows that the required PVC recovery is influenced by the sampling uncertainty. Note that the difference between the required recovery with or without accounting for the sampling uncertainty diminishes for larger numbers of PVC bottles. In general, however, the recovery of PVC by the sorting is required to be high.

CONCLUSION

The principal objective of PET sorting is to reduce the level of PVC below a predetermined level at an early stage of the PET recycling process. Knowledge of the level of PVC in the feedstock for the sorting process and the recovery of PVC achieved by the sorting process helps to understand whether batches of PET with the required quality for further processing can be produced. This is especially critical if the collection process is non-selective and PVC recovery through the sorting process is low and/or variable. The sorting process may not be able to achieve a PET product of the desired quality if the number of PVC bottles in the feedstock is substantial. When relatively high levels of PVC are suspected in the PET feedstock for the sorting process, acceptance sampling of the feedstock may be performed. If the feedstock sample were judged by the maximum tolerated PVC concentration of PET product after sorting, detection of a single PVC bottle in a sample would lead to rejection of the feedstock. Allowing for a higher number of PVC bottles in a feedstock sample requires that the PVC recovery of the sorting process is accounted for. If the uncertainty of sampling the feedstock is also considered, it follows that the sorting process needs to achieve a consistently high recovery of PVC.

REFERENCES

Awaja, F and Dumitru P, 2005. Recycling of PET, *Euro Polymer Journ*, 41:1453-1477.

Bittner, G D, Yang, C Z and Stoner, M A, 2014. Estrogenic chemicals often leach from BPA-free plastic products that are replacements for BPA-containing polycarbonate products, *Environ Health,* 13:1-14.

Commission Directive 2011/8/EU, 2011. Official Journal of the European Union <eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2011:026:0011:0014:EN:PDF>

Constitutional Council Decision no. 2015-480 QPC, 2015. Official Journal of the French Republic http://www.conseil-constitutionnel.fr/conseil-constitutionnel/francais/les-decisions/acces-par-date/decisions-depuis-1959/2015/2015-480-qpc/decision-n-2015-480-qpc-du-17-septembre-2015.144363.html

European Food Safety Authority, 2011. Scientific opinion on polybrominated diphenyl ethers (PBDEs) in food, *EFSA Journ*, 9(5):2156, 274 pp.

European Food Safety Authority, 2015. No consumer health risk from bisphenol A exposure <www.efsa.europa.eu/en/press/news/150121>.

Hopewell, J, Dvorak, R and Kosior, E, 2009. Plastic recycling: challenges and opportunities, *Phil Trans Roy Soc B*, 364: 2115-2126.

Pawlak, A, Pluta, M, Morawiec, J, Galeski, A and Pracella, M, 2000. Characterization of scrap poly(ethylene terephthalate), *Euro Polymer Journ*, 36(9):1875-1884.

Plastics – the Facts, 2016. An analysis of European plastics production, demand and waste data. www.plasticseurope.org/Document/plastics---the-facts-2016-15787.aspx

Rahman, F, Langford, K H, Scrimshaw, M D and Lester, J N, 2001. Polybrominated diphenyl ether (PBDE) flame retardants, *Sci Total Environ*, 275(1-3):1-17.

Scott, D M, 1995. A two-color near-infrared sensor for sorting recycled plastic waste, *Measurement Sci Technol*, 6:156-159.

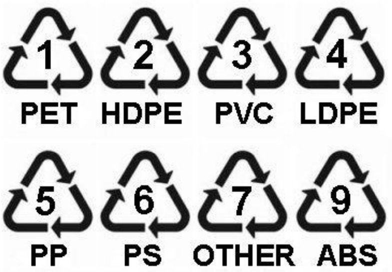
Stichting Retourverpakking Nederland, 2016. www.retourverpakking.nl

Tachwali, Y, Al-Assaf, Y and Al-Ali, A R, 2007. Automatic multistage classification system for plastic bottles recycling, *Res Conserv Recyc*, 52(2):266-285.

vom Saal, F S, Cooke, P S, Buchanan, D L, Palanza, P, Thayer, K A, Nagel, S C, Parmigiani, S and Welshons, W V, 1998. A physiologically based approach to the study of bisphenol A and other estrogenic chemicals on the size of reproductive organs, daily sperm production, and behaviour, *Toxicol Ind Health*, 14:239-260.

Welle, F, 2011. Twenty years of PET bottle to bottle recycling - An overview, *Res Conserv Recyc*, 55:865-875.

Widén, H, Leufvén, A and Nielsen, T, 2005. Identification of chemicals, possibly originating from misuse of refillable PET bottles, responsible for consumer complaints about off-odours in water and soft drinks, *Food Add Contam*, 22:681-692.



1 PolyEthyleneTerephtalate (PET, or PETE)
2 High Density PolyEthylene (HDPE)
3 PolyVinylChloride (PVC, or V)
4 Low Density PolyEthylene (LDPE)
5 PolyPropylene (PP)
6 PolyStyrene (PS)
7 any other plastic (OTHER, or O)

Figure 1: Plastic type identification codes (www.plasticsindustry.org)

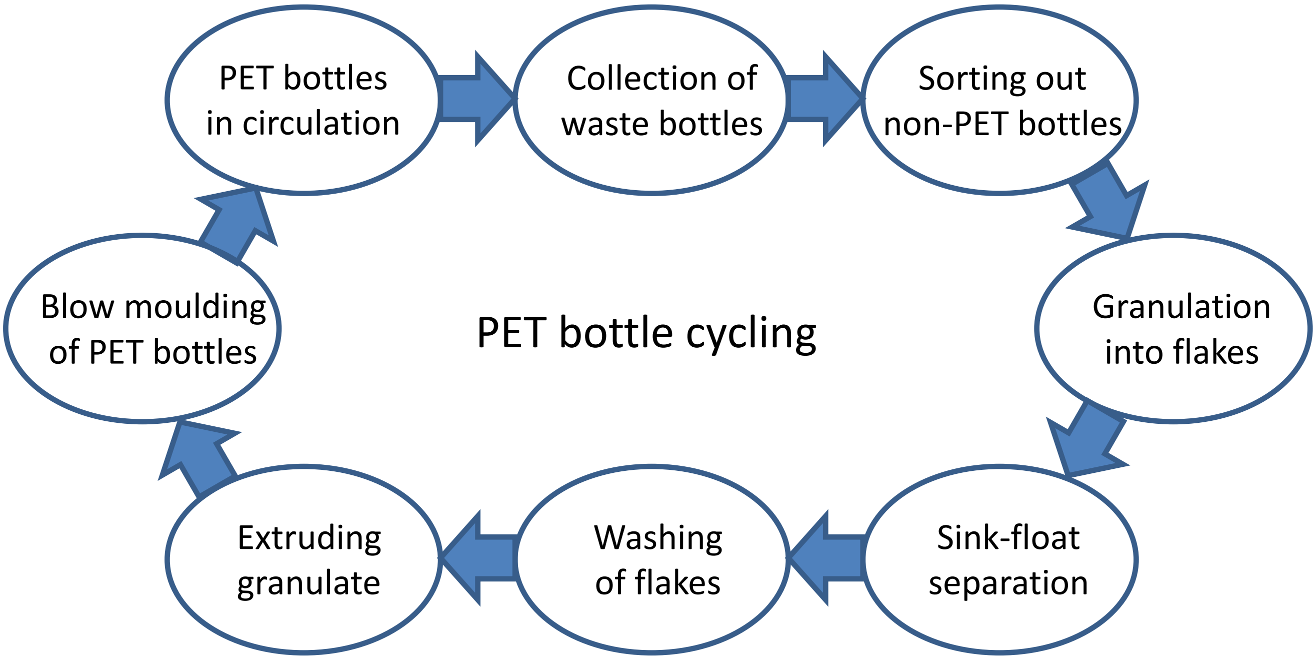


Figure 2: Typical flowsheet of single-use PET bottle recycling

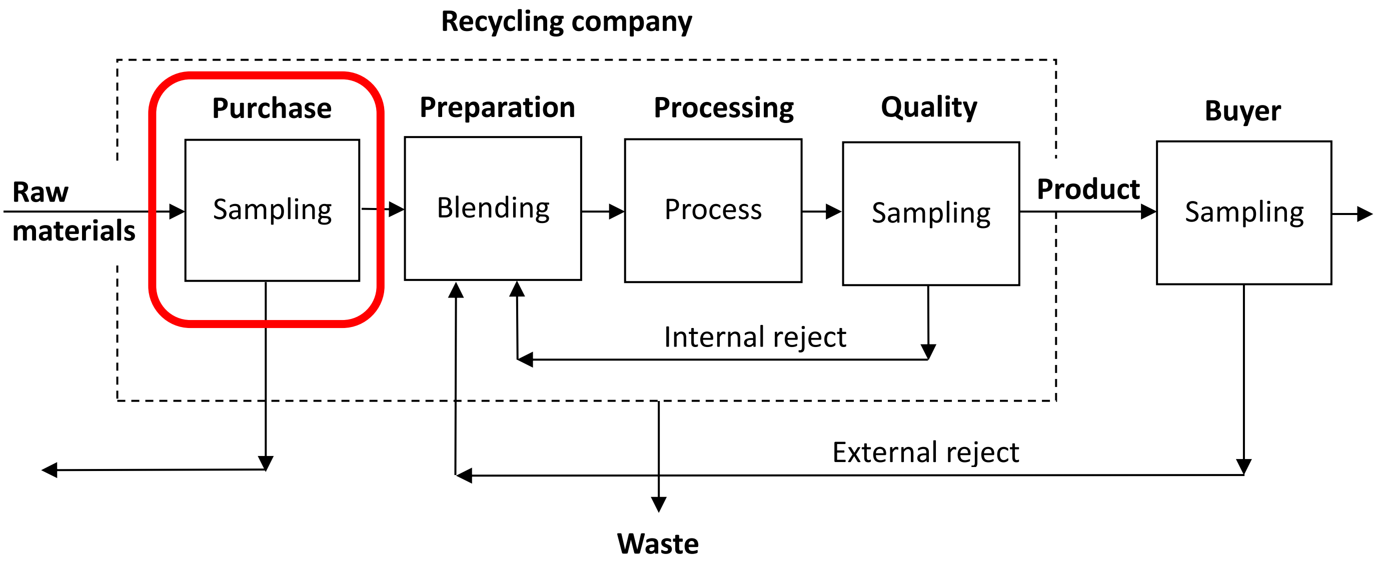


Figure 3: Schematic overview of possible sampling and blending points in a recycling company. Acceptance sampling of bales of waste plastic bottles may take place at the point of entry into the recycling company. After possible blending, any non-PET bottles are separated with a suitable sorting process.

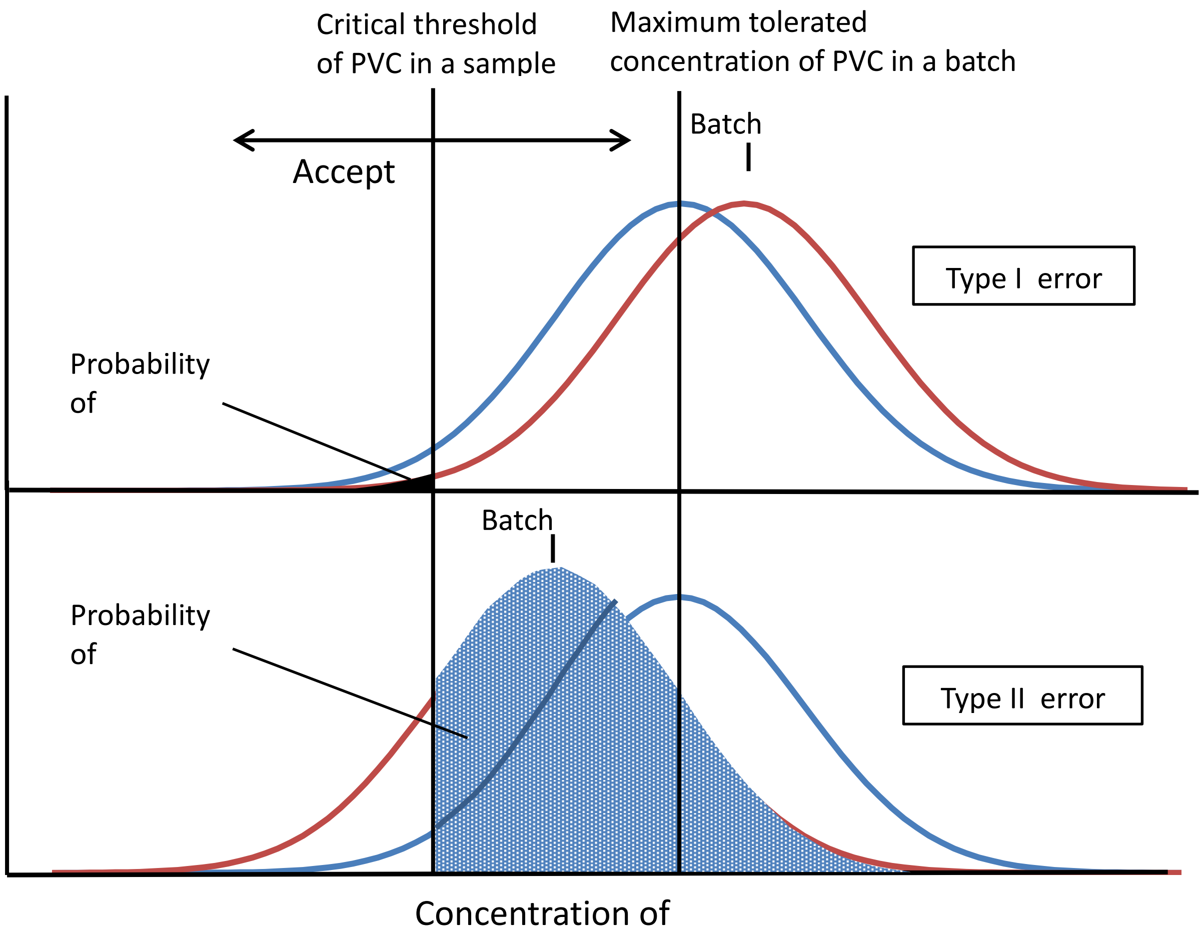


Figure 4: Decision-making based on analysis of a single sample of PET bottles. A sampling distribution is constructed about the maximum tolerated concentration of PVC in a batch of PET. This distribution is used to establish the critical threshold concentration of PVC in a sample of PET. The sampling distribution of two batches of PET with different concentrations of PVC is also shown, illustrating the probability of a type I error in the upper section of the figure case and the probability of a type II error in the lower section of the figure.

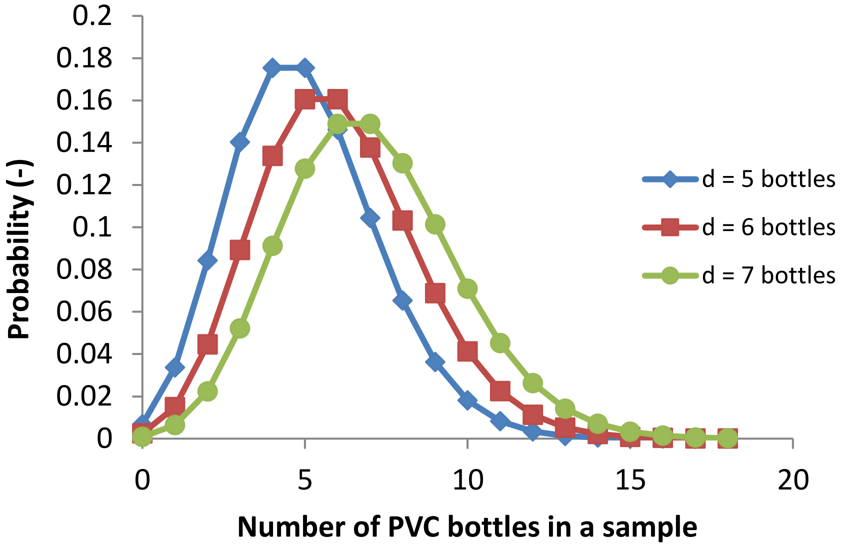


Figure 5: Transition of the Poisson distribution towards the Gaussian distribution for sampling distributions about different numbers (d) of PVC bottles.

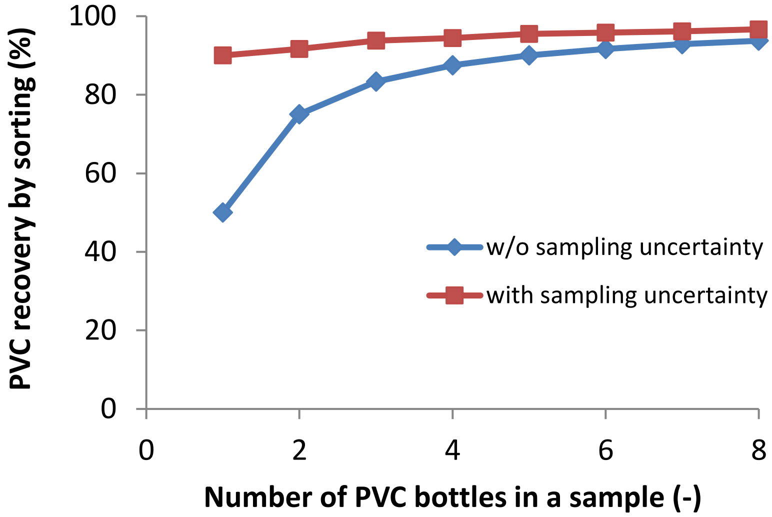


Figure 6: Required recovery of PVC bottles by a sorting process as part of recycling of single-use PET bottles.