Analytical issues in the assessment of waste stabilisation degree after biological treatment

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Please cite as: CHEMIK 2012, **66,** 11, 1211-1218

Introduction

The European legal regulations (European Landfill Directive, EC/99/31) [1] stipulates the requirement to reduce the volume of biodegradable waste stored on landfills. The Directive sets forth the plan of reduction of the share of organic matter in waste deposited on landfills. Pursuant to EU policy, as of 1January 2013, prior to emplacement on landfill, the waste will have to be treated and meet the applicable quality norms, such as degree of stability [2]. Directive EC/99/31 does not provide the methods for assessing the waste stability. Some Member States have their own regulations addressing this matter. Works are in progress on unifying the methodology and establishing the limit values for the bioactivity of waste landfilled in the European Union. There are various tests available to determine the bioactivity of waste [3]. Jędrczak [4] reports that the draft of the Directive on "Biological treatment of waste" sets forth the requirement to determine the respiration activity (AT-4) of waste after mechanical and biological treatment, or the dynamic respiration index (DRI). Germany and Austria have introduced the requirement to assess two parameters of biological stability of landfilled waste (AT-4 and GS21). In Poland work is in progress to meet the relevant requirements set forth by the EU. The Polish law assumes gradual reduction of landfilled waste and the reduction of the biodegradable fraction share in the waste. In 2008 the Department of Waste Management of the Ministry of Economy published the "Guidelines on the requirements for composting, fermentation and mechanical and biological treatment of waste" [5]. The authors of the document proposed using the methodology from the Austrian norm [6]. Unfortunately, the plan to implement in Polish laboratories the measurement of AT-4 as the waste stabilisation parameter supplementary to the ignition loss and TOC in 2009÷2010 was never carried out. On the basis of the guidelines a draft of the Ordinance of the Minister of Environment of 14 March 2012 was prepared, concerning the mechanical and biological treatment of mixed municipal waste [7]. The draft includes a provision on the requirement to assess the AT-4 parameter for waste undergoing aerobic biological treatment. The acceptable value for this type of waste would not exceed 20 mgO_2/g of dry mass. Prior to landfilling the stabilised compost should meet the applicable quality requirements, such as ignition loss <35% of dry mass, TOC <20% of dry mass, loss of organic matter or TOC >40% of dry mass, and AT-4 <10 mgO_2/g of dry mass. The draft also stipulates that the collection of samples and testing of relevant parameters should be performed by an accredited laboratory or a laboratory with a certificate of implemented quality management system. At the moment Polish laboratories are not equipped to introduce this parameter into the standard testing procedures. The assessment of the AT-4 parameter is not a simple task. Analytical issues occur frequently during tests. A further obstacle for the introduction of this parameter is the absence of national norms, training bodies or problems with equipment purchase. In Austria the government reference body for waste treatment and assessment of AT-4 is the Waste Management Institute in Vienna (Institut für Abfalwirtschaft, Universität für Bodenkultur, Wien), with Dr Erwin Binner as the leading expert in the field. Basing on Austrian expertise and own research, this paper outlines the most frequent analytical issues occurring in the assessment of AT-4 [8÷10].

Analysis of AT-4 parameter

The AT-4 parameter assessment method comprises the measurement of O_2 consumption during the decomposition of the organic fraction of waste. In the course of many years of experiments in Germany and Austria the conclusive analysis parameters have finally been determined [11, 12]. Among others, the experiment duration has been established. With the linear course of the process in time, the parameter can be assessed already after 4 days. This paper outlines the Austrian methodology [6], as recommended by the "Guidelines…" [5].

Collection of samples

Waste is collected from piles made from biologically treated waste. The Austrian norm [6] provides the method of sample collection from piles. According to the norm, three qualified primary samples should be collected. A single qualified primary sample includes at least 10 primary samples collected from the pile. The required weight of the primary samples for granulation <40 mm is approx. 2.5 kg (approx. 5 l). Primary samples are collected from the entire pile. The three qualified primary samples are mixed with each other. Using the quartering method, from the mixed qualified primary samples one working sample is obtained, with the volume of approx. 50 l. The working sample is delivered to the laboratory and minced until the granulation is <20 mm. The required volume of the laboratory sample is approx. 10 l. The remaining part is categorised as archive sample and stored until the completion of the test. Incorrect collection of the sample may result in problems with the assessment of the AT-4 parameter and thus it may produce false results. The problems that may occur during sample collection include mainly the absence of piles or irregular forking over of the piles, which results in inhomogeneity and putrefaction of the waste material. Improper aeration of the waste material on landfill results in understated AT-4 value. It should be pointed out here that samples should be collected by properly trained employees, using appropriate equipment. The samples should be delivered to the laboratory within 48 h after collection. If it is impossible, the samples should be frozen and stored at -18°C (-20°C).

Sample preparation

Samples are minced (<20 mm) in special cutters that do not crush or heat up the material. The prepared samples are wetted. The previously applicable Austrian norm provided a wetting method

in which 300 g of waste material was mixed with 300 ml of water and then the mixture underwent vacuum filtration. In the current norm, the Austrians do not provide the wetting method. Dr Binner uses the *fist test* method, i.e. he squeezes the wetted sample in his palm. The resulting "roll" should not fragment on open palm. When squeezed, water should not flow from the sample. The samples that are too dry should be wetted, while those too moist should be pressure-filtered. Incorrect wetting of the sample will produce understated results. It should be noted that fist testing method may be hazardous in case of municipal waste which might contain sharp elements. Therefore, the laboratory should determine its own method for assessing the wetting of the sample. In Austria wetted samples are left in closed containers for 12-24 h in order to trigger the microbiological decomposition. In certain cases samples are additionally aerated before analysis. Aeration might last from several to several dozen hours. The prepared waste is weighed and transferred into testing apparatus. In the case of frozen samples, they should be slowly thawed for 24 h at 20°C before analysis. Otherwise, the final result will be unreliable.

Apparatus for assessing the AT-4 parameter

The AT-4 parameter is usually assessed using SAPROMAT or OxiTop apparatus. The analysis is repeated at least twice.

The SAPROMAT kit (Photo 1) comprises a reaction vessel, CO_2-absorbing compound, electrolyser to produce oxygen consumed during the process, and manometer. The kits are placed in a water bath at 20°C and connected to the oxygen feeding controller and PC collecting the measurement data. The advantages of this device include automatic oxygen feeding, continuous operation and data collection. Despite full automation, the apparatus should be monitored during analysis due to possible disruptions, e.g. in oxygen production. The disadvantage of this apparatus is its unavailability on the Polish market, forcing the potential users to purchase the device and spare parts abroad. Also, the purchase and operation costs are high.

The OxiTop (Photo 2) is less complicated that SAPROMAT. It comprises a number of separate vessels, hermetically closed with covers fitted with negative pressure sensors. CO_2 absorbent is placed inside the device. Vessels are incubated at 20°C in thermostatic cabinet. The sensor located on top of the vessel enables pressure readouts every 28 minutes. The data on the negative pressure created in the vessel and recorded by the sensors are collected by means of the controller and converted into the volume of consumed oxygen. During the analysis, the vessel should be opened manually to aerate the sample. The results are usually collected within 7 days. Then, the so-called lag phase and actual analysis time is calculated (4 days). Sometimes tests are performed over a dozen days for samples that initially exhibit very low oxygen consumption (only a few mgO_2/g of dry mass). The point of this prolonged analysis is to see whether activity will suddenly rise after a long lag phase. Therefore, the need to continuously aerate the sample or read the data forces the analysts to work also on weekends. The main disadvantage of OxiTop, as with SAPROMAT, is the unavailability of this apparatus on the Polish market. Even though there are similar devices available, used for assessing BZT5 with negative pressure analysis, there are no vessels with the required capacity for AT-4 (2 litres). During the analysis the tightness of the vessels should be carefully monitored. Leaks may be caused by incorrect placement of gaskets or incorrect closing of the vessel, especially given the fact that vessels are frequently opened and closed during aeration. A further obstacle is the need to continuously read the data and control the course of the process in order to determine the frequency of aeration. Very active samples should be aerated more frequently (a couple of times a day), while less active samples may be aerated less often. With a too rapid course of the process the risk of insufficient sample aeration occurs. This produces understated results. Before starting the analysis, the analyst should have comprehensive knowledge on the origin of the analysed material in order to estimate its activity. Otherwise, the analyst might make a mistake in determining the weighed amount, the duration of the lag phase or the frequency of aeration. The key factor in correct analysis is thus the analyst's experience.

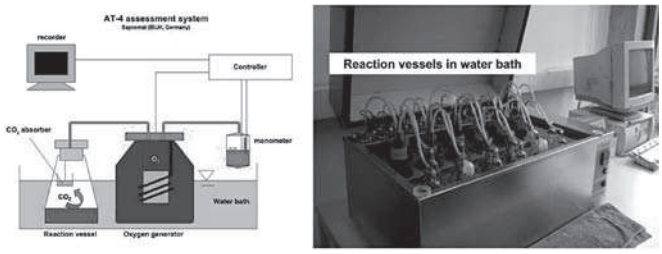

Photo 1. Analysis workflow and the SAPROMAT apparatus

Photo 2. OxiTop vessels containing samples, absorbent and negative pressure sensors. Data readout using the controller

Analysis with OxiTop

Usually 40g of wetted sample are weighed out, with accuracy to 0.1 g. In the case of very active samples, the weighed amount may be reduced and the reduction included in the calculations. Before starting the analysis, the analyst must know the origin of the waste in order to estimate its reactivity and determine the weighed amount. The analysed sample is placed in the reaction vessel, containing the CO_2 absorbent. The absorbent is usually sodium hydroxide, potassium hydroxide or calcium hydroxide. It is recommended to use absorbents with an indicator to enable visual assessment of absorbent consumption. If the absorbent runs out, CO_2 will no longer be absorbed, the negative pressure will be reduced and, in consequence, the final result will be distorted. After assembling the kit, the negative pressure created from adsorbed CO_2 is measured. The AT-4 value is determined within 96 hours from the end of the lag phase. According to the Austrian norm, the lag phase ends when the mean for a 3-hour measurement reaches 25% of the maximum oxygen demand. It is calculated from the data obtained from 5÷7 days of the process. Also, the actual analysis time is determined (4 days) then. The read values are keyed into appropriate software which converts them into 3-hour means and plots a diagram of the correlation between the total oxygen consumption and the process duration. Figure 1 provides the example diagram of oxygen consumption over time, with marked lag phase and determination of the AT-4 parameter. The result is provided in mg of O_2 per gram of dry mass, with the accuracy to at least two significant figures. The assessment of the actual lag phase duration and AT-4 readout is performed by the analyst. Ultimately, it is the analyst who decides on the final result value.

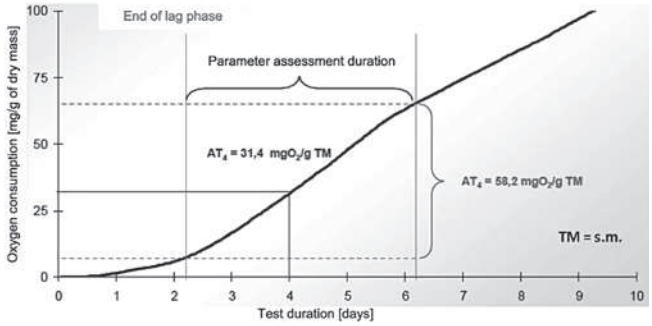

Fig. 1. Example diagram of oxygen consumption over time, with marked lag phase and determination of the AT-4 parameter; T.M. (total dry mass) = s.m. (dry mass). Source: training materials, Binner E., Vienna 2011 [10]

Aside from analytical issues, the assessment of the AT-4 parameter might be distorted by other factors. For instance, the sample might contain toxic substances. Those include heavy metals, detergents or organic solvents that inhibit microorganism growth and understate the final result. In Austria samples with particularly high toxin content or very low AT-4 value are additionally enhanced with glucose. Then, a particularly high rise in activity might indicate the presence of toxins in the analysed material (Fig. 2). Furthermore, too high or too low sample reaction produces an understated result. In Austria the pH value of the material is adjusted to approx.7 in order to unify the analysis conditions. Samples with too high or too low pH values are characterised by very low AT-4 value (<7 mgO_2/g of dry mass) and the lag phase might take as long as several days (Fig. 3). When the sample is neutralised, the process runs efficiently. Also sample hypoxia before analysis might affect the results. In Austria the putrefied samples undergo pre-aeration in order to facilitate the growth of aerobic microorganisms. Insufficient pre-aeration of the sample before analysis produces an understated result (Fig. 4). At the final stage of analysis the dispersion of results from two repeats might be too high. In such cases the analysis should be repeated using archive samples and the results compared again.

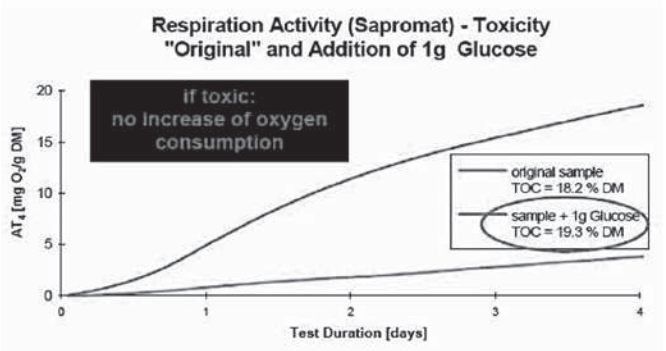

Fig. 2. The impact of toxins on respiration activity (AT-4) of the original sample and after addition of medium (glucose). Source: training materials, Binner E., Vienna 2011 [10]

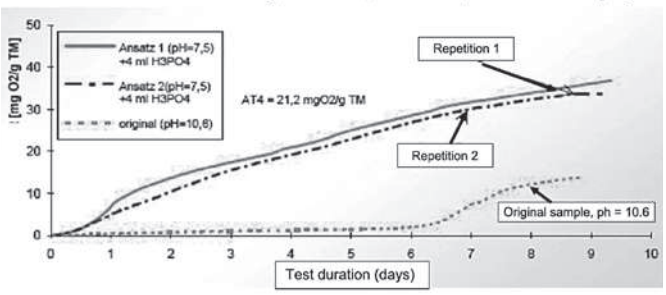

Fig. 3. The impact of pH of the sample on respiration activity (AT-4). The pH value of the original sample was 10.6, after neutralisation with H_3PO_4 pH was adjusted to 7.5. Lag phase for the original sample was 6 days and for the neutralised sample – 1 day. Source: training materials, Binner E., Vienna 2011 [10]

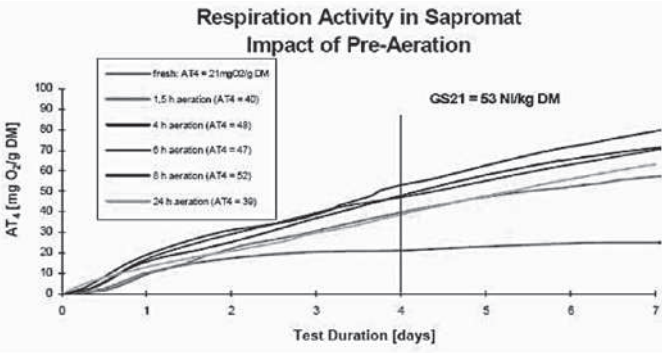

Fig. 4. The impact of pre-aeration of the sample on respiration activity (AT-4). The original sample is marked in red. This sample was characterised by the lowest AT-4 value. Subsequent plots indicate the course of reaction for the same sample, undergoing pre-aeration at different points in time Source: training materials, Binner E., Vienna 2011 [10]

Summary

The most frequent issues, directly impacting the final result, include:

- incorrect collection of samples, insufficient training of collectors
- no forking over of the piles, no waste screening, too large objects
- incorrect sample mincing before analysis (<20 mm), potential heating of samples during mincing
- failure to deliver the sample to the laboratory within 48 h
- incorrect freezing and thawing of samples, no archive samples
- incorrect sample hydratation before analysis
- no pre-aeration of putrefying samples before analysis
- incorrect operation of the equipment, no control of tightness, consumption of reagents and other
- insufficient sample aeration during analysis due to the need to manually aerate and read results (OxiTop)
- insufficient time of analysis and data collection and the resulting incorrectly determined lag phase
- no information on the origin of the sample and incorrect visual assessment of the material by the analyst, resulting in incorrectly estimated material reactivity
- incorrect sample reaction, impact of toxins, resulting in incorrectly determined lag phase and understated result
- incorrect averaging of results characterised by high dispersion between repetitions.

High number of potential analytical issues during the assessment of the AT-4 parameter may lead to unreliable results. The norm in Polish is still yet to be developed. It has been suggested to implement the guidelines from the Austrian norm in Poland. However, the Austrians continually verify their norm and amend the applicable methodology. Furthermore, there are no companies on the market to sell the testing and auxiliary equipment, e.g. mills with appropriate parameters. The cost of purchasing and importing the equipment from abroad is very high. Another issue is the absence of experienced training personnel. It should be pointed out that the AT-4 parameter should be assessed by accredited laboratories. The laboratories in Poland are not equipped to conduct analysis on this level due to the absence of appropriate apparatus, experienced personnel and lack of certified reference materials on the market or the unavailability of comparative analysis between laboratories. Exporting samples abroad in order to assess the AT-4 parameter does not appear to be the solution, either. Therefore, an alternative method for assessing the susceptibility of landfilled waste to biological decomposition should be developed. Cossu and Raga [13] suggest that ChZT-Cr and BZT-5 parameters in aqueous extracts are correlated with AT-4 and thus sufficient to determine the waste susceptibility to decomposition. At the moment it is difficult to make any conclusive predictions as to what will happen

after the requirement to assess the AT-4 parameter is introduced in Poland. However, everything remains in the hands of the legislator. It is important for the draft of the new law to take the specific Polish conditions into consideration.

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- Philip Lane, Head of Fungicides Research and Development, Crop Protection, BASF SE –Technological cooperation in crop protection discovery
- Malcolm Faers, Bayer CropScience AG – Looking inside the spray deposit: towards a deeper understanding for tomorrow's advanced flowable formulations
- Harald Walter, Research Portfolio Manager, Fungicides, Syngenta – Innovation in the seed care segment: Sedaxane fungicide, a case study on chemical and biological aspects
- David Ager, Principal Scientist, DSM Innovative Synthesis BV – Outsourcing agrochemical intermediates and ingredients – the CMO's perspective
- Nigel Uttley, Managing Director, Enigma Marketing Research – Barriers to market entry for generic agrochemical companies
- Rob Bryant, Managing Director, Agranova – Agrochemical pest control – new active ingredients are still needed
- Peter Chapman, Director of Regulatory Affairs, JSC International will chair the discussion group 'Commercialisation of new agrochemicals: addressing regulatory aspects'
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