

# Application Note XE1

## Microwave Digestion of Wastewater according to EPA 3015A

### Summary

A sample preparation method of wastewater for elemental analysis is introduced below. Wastewater samples are digested using speedwave XPERT in various vessel systems according to EPA Method 3015A. During the digestion, the reaction temperature and pressure are controlled via contactless in-situ temperature sensor (DIRC) and pressure sensor (OPC) to ensure efficient digestion. The applicability of various vessel types for the EPA 3015A method and the necessity of the OPC for eliminating undesired overpressures are explained.

### Introduction

Hazardous Waste Test Methods/ SW-846 are approved procedures for qualitative and quantitative determination of physical and chemical pollutants. Office of Solid Waste of the US Environmental Protection Agency (EPA) publishes these methods to serve a guidance for applying appropriate analytical procedures.

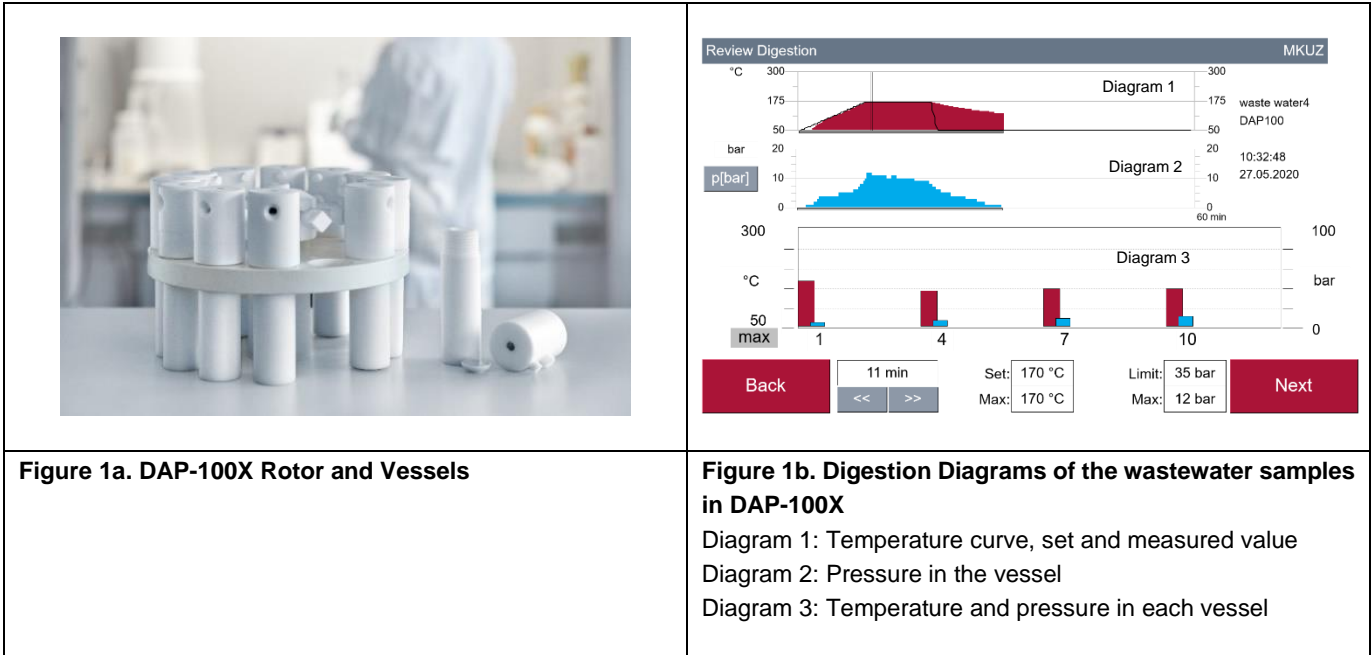
EPA 3015A is one of these methods which is used for aqueous samples and extracts, drinking water and wastewater that can contain suspended solids. The aim is to extract elements, such as Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, Pb, Sb, Se, Sr, Ti, V, Zn from the aqueous samples by conducting microwave heating at  $170 \pm 5$  °C in acidic medium. The method does not guarantee a complete decomposition but provides a reliable acid leaching for the samples.

Users will find the pre-installed temperature program for EPA Method 3015A in speedwave XPERT. It is crucial to note that analysts may need to optimize the method for their own samples depending on the reactivity of their samples and vessel systems. Therefore, this application note shows an optimization approach for digesting wastewater samples by using various vessel types, in-situ temperature sensor (DIRC) and pressure sensor (OPC).

### Instrumentation

	Rotor and Vessel Type	Liner Type	
Microwave Digestion	<input type="checkbox"/> DAP-40X		<input type="checkbox"/> MiniVessels
	<input checked="" type="checkbox"/> DAP-60X	<input type="checkbox"/> DAQ-20H	<input type="checkbox"/> MiniVessels
	<input checked="" type="checkbox"/> DAP-100X	<input type="checkbox"/> DAQ-22H	<input type="checkbox"/> DAC-17
	<input checked="" type="checkbox"/> DAK-100X		<input type="checkbox"/> MultiTube
			<input type="checkbox"/> MiniVessels

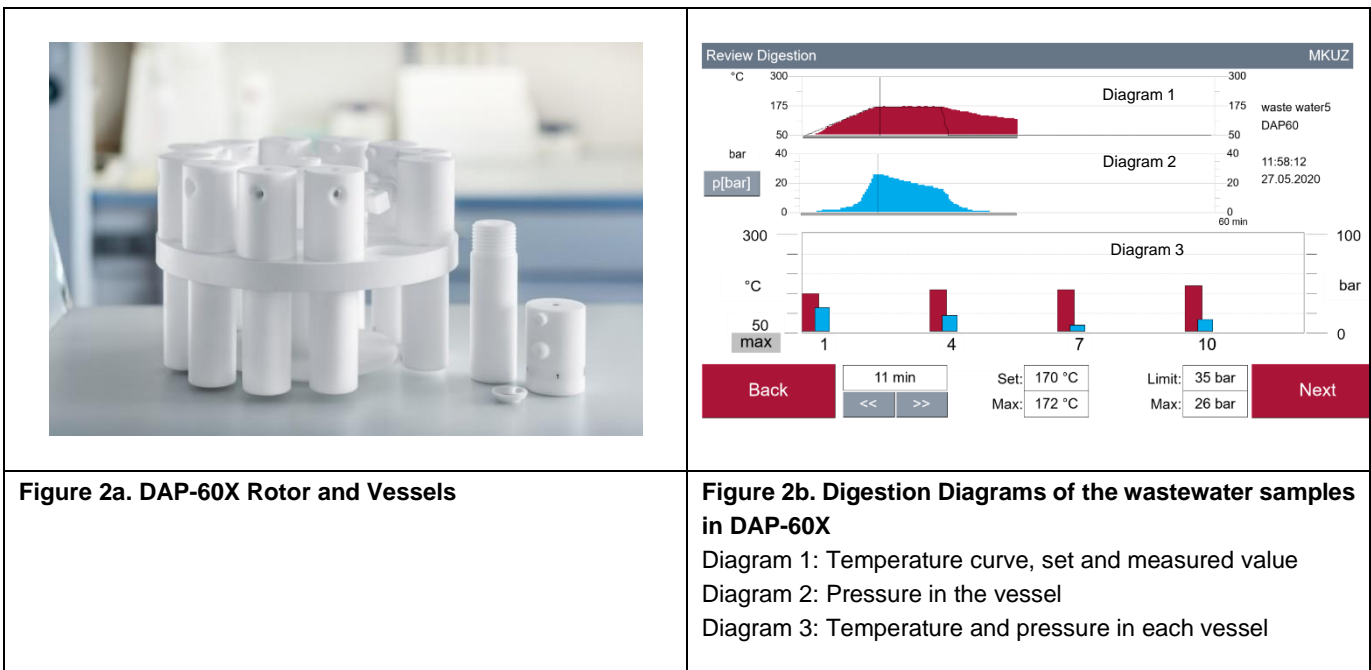
Procedure						
<b>Sample Amount</b>	45 ml for DAK-100X and DAP-100X; 35 ml for DAP-60X					
<b>Sample Preparation</b>	Wastewater samples are collected in pre-washed plastic bottles and acidified to a pH < 2 with HNO <sub>3</sub> before storage.					
<b>Reagent/s</b> <sup>[2]</sup>	5 ml HNO <sub>3</sub> (65%) or alternatively 4 ml (65%) and 1 ml HCl (37%)					
<b>Experiment</b>	<p>Measure an aliquot of sample into the digestion vessel. Add the reagent/s. Swirl the mixture carefully or stir with a clean PTFE or glass bar. Keep the vessel in the fume hood at least 10 minutes for pre-reaction. In case of vigorous reaction, increase the pre-reaction duration. Seal and close the vessels as described in the operation manual. Start the digestion according to the following temperature program. Allow the vessels to cool down to room temperature and open them carefully as described in the operation manual. <sup>[1]</sup> If particulates are present in the sample, filter or centrifuge the sample. Transfer the sample into centrifugal tubes for appropriate elemental analysis.</p>					
<b>Temperature Program</b> <sup>[2]</sup>	<b>Step</b>	<b>T [°C]</b>	<b>p [bar]</b> <sup>[3]</sup>	<b>Ramp [min]</b>	<b>Hold [min]</b>	<b>Power [%]</b> <sup>[4]</sup>
	1	170	35   60	10	10	80
	2	50	35   60	1	10	0
<b>Results</b>	Clear and colorless solutions.					
<b>EPA 3015 Requirements for vessels and sensors</b>	<p>As required in the EPA 3015A;  <sup>[1]</sup> All our vessels are microwave transparent and reagent resistant materials.  <sup>[2]</sup> The internal volume of the DAK-100X and DAP-100X vessels are 100 ml while volume of DAP-60X is 60 ml.  <sup>[3]</sup> All the vessels are able to withstand pressures of at least 30 bar and able to relief overpressures. Specifically, DAK-100X is capable of pressures up to 100 bar, while DAP-100X and DAP-60X are up to 40 bar.  <sup>[4]</sup> In-situ temperature sensor (DIRC) and pressure sensor (OPC) provide temperature and pressure control in each vessel.</p>					
<b>Discussion   DAP-100X</b>	<p><b>Figure 1a and 1b</b> represent DAP-100 vessel system and corresponding digestion diagrams for wastewater, respectively. Contactless in-situ temperature sensor (DIRC) controls the temperature inside each vessels. The digestion temperature of 170 °C is efficiently reached and applied for 10 minutes as suggested by the EPA Method 3015A (<b>Diagram 1, Figure 1a</b>). Optical pressure sensor (OPC) allows us to monitor the pressure in each vessels. This measurement is crucial to prevent overpressures resulting from the formation of gaseous reaction products and vapor pressure of the medium. In case of undesired pressures (pressures above the pressure limit given in the temperature program), the microwave will reduce the power and reaction temperature to keep the pressure below the limit.</p> <p>EPA Method 3015A provides a temperature and pressure profile for a simulated sample containing ~0.35 g of SRM 2704 + 45 ml double deionized water that shows digest pressures of 13 to 8 atm at 170 °C in 100 ml vessel (please see EPA Method 3015A). Similar pressures of 12 to 8 bar at 170 °C are monitored in our wastewater samples (<b>Diagram 1, Figure 1a</b>). The water only pressure shows ~7 bar which is the vapor pressure of water please see EPA Method 3015A).</p>					



**Discussion | DAP-60X**

In case of using DAP-60 vessels (**Figure 2a**), one should reduce the sample amount not to stress the vessels in long-term usage. To illustrate, we digested the same wastewater samples in DAP-60 vessels by reducing the volume of the sample from 45 ml to 35 ml. **Figure 2b** represents the digestion of the samples at 170 °C with a maximum pressure of 26 bar. Reducing the sample amount reduces the pressure as expected by the Boyle's Law. This optimization will save your vessels in long-term and eliminate any unexpected overpressures due to sample varieties.

As can be seen in temperature profiles of 4 samples in DAP-100 (**Figure 1b, Diagram 3**) and DAP-60 (**Figure 2b, Diagram 3**), we monitored homogeneous temperature distribution. Depending on the content of the wastewater samples, monitored pressures can vary from sample to sample. For example, wastewater samples containing high carbon or organic content will create higher pressures due to the formation of more gaseous digestion products. In case of digesting such aqueous samples with high carbon content, one may reduce the sample size, such as 10-15 ml until monitoring pressures below 30-35 bar. Another approach may be diluting the highly contaminated wastewaters as suggested by the EPA Method 3015A. This approach can be done until observing pressures below 30-35 bar in DAP-100 or DAP-60 vessels.



**Discussion | DAK-100X**

Using DAK-100 vessels (**Figure 3a**) for digesting highly contaminated wastewaters may serve another solution due to high-pressure capabilities of these vessels. **Figure 3b** represents the digestion diagram of wastewater samples in DAK-100. Similar digestion pressures are observed as in the case of DAP-100. In case of expecting more than 40 bar of pressures, one can use DAK-100 vessels by conducting the experiments according to the EPA Method 3015A. As in the case of DAP-100 and DAP-60, DIRC and OPC will control the temperature and pressure in each vessels. If the pressure reaches higher values than the limit given in the temperature program (such as 60 bar), speedwave XPERT will regulate the power to keep the pressure below this limit.

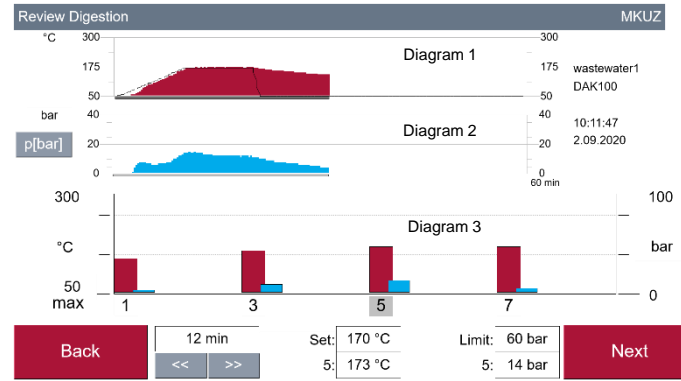
**Figure 3a. DAK-100X Rotor and Vessels****Figure 3b. Digestion Diagrams of the wastewater sample in DAK-100X**

Diagram 1: Temperature curve, set and measured value

Diagram 2: Pressure in the vessel

Diagram 3: Temperature and pressure in each vessel

**Conclusion**

To conclude, this application note demonstrated the ability of the speedwave XPERT and various vessel systems to apply EPA Method 3015A for wastewater samples. Controlling the temperature and pressure optically by DIRC and OPC are crucial to ensure efficient digestions.

**Reference**

- [1] <https://www.epa.gov/hw-sw846>  
 [2] <https://www.epa.gov/sites/production/files/2015-12/documents/3015a.pdf>

**Notes**

- [1] To avoid foaming and splashing wait until the vessels have cooled to room temperature (about 20 min). Carefully open the digestion vessel in a fume hood wearing hand, eye and body protection since a large amount of fumes will be produced during the digestion process.  
 [2] This application serves only as a guideline and may need to be optimized for your sample.  
 [3] Pressure is the maximum value given to the program that is limited by the vessel and / or rupture disc specifications.  
 [4] This application is outlined for 4 digestion vessels. Increase or decrease the power by 10% per sample, when using more or less sample. Minimum is 40% independent of the sample number.