

## Application Note 150

# Addressing the challenges of microplastic characterisation using thermal desorption

### Summary

In this application note, we demonstrate the quantitative analysis of microplastics using direct thermal desorption (TD) combined with gas chromatography–mass spectrometry (GC–MS). Direct desorption of filtrates containing microplastics provides a simple and streamlined sample preparation step while GC–MS analysis produces information-rich volatile organic compound (VOC) profiles. The VOC profiles contain marker compounds to identify and quantify the plastic, along with other chemical signatures that could prove useful in source apportionment, toxicity assessment and regional profiling.

Analysis of polyethylene terephthalate (PET) particles from bottled drinks is shown to deliver fast, reproducible, quantitative results, providing plastic concentrations in µg/L for particles as small as 0.3 µm in diameter.

### Introduction

Microplastics have been found to pollute our oceans, soil, air, drinking water and food. They are defined as particles or polymeric fibres 1 µm to 5 mm<sup>1</sup> in diameter and come from a range of sources including clothing, bottles, food packaging, toys and vehicle tyres.

The potential threat to the environment and human health is driving the need for the standardised measurement and regulation of microplastics. In January 2019, ECHA (the European Chemicals Agency) proposed a restriction on the intentional use of microplastics in products placed on the European Union/European Economic Area market to avoid or reduce their release into the environment.<sup>2</sup> The proposal is currently at the consultation phase.

A report by the World Health Organization (WHO), published in the same year, examines evidence related to microplastics in the water cycle (including tap and bottled water and its sources), the potential impact on health after exposure to microplastics and the removal of microplastics during wastewater and drinking water treatments.<sup>3</sup> In the report, the WHO includes recommendations for taking action such as monitoring and managing microplastics in the environment.

Currently, there are no standardised methods for the characterisation of microplastics, and the scientific community and regulatory bodies are evaluating a number of different techniques. It is unlikely that one analytical technique alone will provide the full picture for microplastics and researchers may require a toolkit of instrumentation spanning spectroscopic and chemical analysis methods. A

chemical analysis method for microplastics should allow the type and amount of plastic to be quantified and ideally provide additional information on polymer additives and absorbed contaminants for source apportionment and toxicity measurement. The method should also be applicable to a wide variety of sample matrices and scalable to widespread environmental testing programmes in the future.

Of the techniques being trialled for microplastics analysis, most typically involve extensive filtration and sample preparation steps followed by analysis using counting techniques such as Fourier-transform infrared spectroscopy (FTIR) or thermal degradation of a sample using pyrolysis. Multiple sample preparation steps followed by transfer of samples to other vessels for analysis can lead to sample losses and introduce manual handling errors – a simpler sample preparation method would minimise these risks. Other limitations include techniques that can only tell us which types of microplastics are present in a sample, not their concentrations, and some spectroscopic techniques are limited to particles greater than 10 µm and some involve lengthy sample preparation procedures (hours to days).

Thermal desorption – one of the sample preparation techniques under consideration – can reduce the number of sample preparation steps and removes the need to transfer the microplastics from the filter to a secondary vessel, so avoids the sample losses and handling errors of other methods. Also, for the majority of filters, TD analyses the entire filtrate rather than a portion of it, which is common with pyrolysis and other chemical analysis techniques. Thus, TD offers maximum sensitivity and avoids the challenge of obtaining a fully representative sample from an inhomogeneous filtrate.

In this application note, we will show how direct TD provides a straightforward, robust, time-saving sample preparation method, applicable to a wide range of matrices and polymer types. Combined with GC–MS, it delivers a VOC profile rich in information about the polymer, its source and the environment it has been exposed to. Quantitative analysis of polyethylene terephthalate (PET) in bottled beverages demonstrates the power of the technique for measuring levels of target plastics, while identification of plastic additives and signatures associated with the beverages within the same data show how VOC signatures can build a comprehensive picture of microplastics, maximising the information gained from a single sample analysis.

## Background to thermal desorption

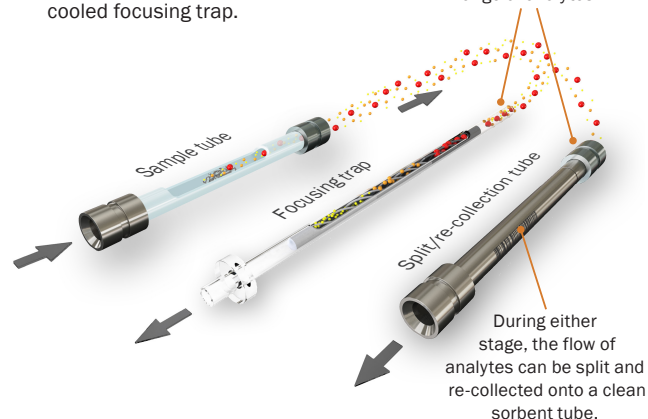
Thermal desorption is a GC preconcentration technique to analyse volatile and semi-volatile organic compounds (VOCs and SVOCs) in a wide range of sample types. By concentrating organic vapours from a sample into a very small volume of carrier gas, TD results in narrow chromatographic peaks, which maximises sensitivity for trace-level target compounds. It also helps to minimise interferences, and greatly improves sample throughput by allowing full automation of sample preparation, desorption/extraction, preconcentration and GC injection.

Typically, TD is a two-stage process (Figure 1). The first stage involves collection of the air/gas sample onto a sorbent-packed tube, which is then heated gently in a flow of inert carrier gas that sweeps the volatiles into an electrically-cooled focusing trap. In the second stage, the focusing trap is heated rapidly, which causes the volatiles to be injected into the GC column in a sharp band of vapour. Solid samples, such as microplastics, can simply be placed into an empty TD tube in the first stage – a process called direct desorption. It is worth noting that this protocol significantly reduces sample preparation time.

### 1. Tube desorption and inlet split:

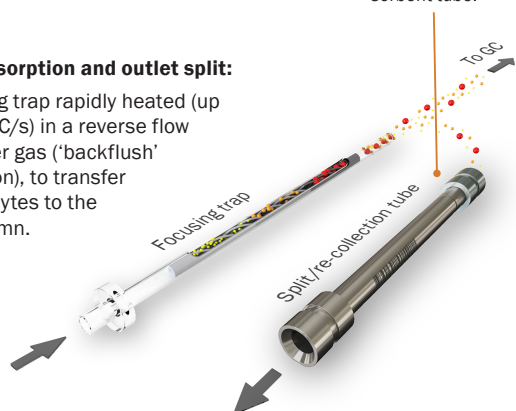
Sample tube heated in a flow of carrier gas and analytes swept onto an electrically cooled focusing trap.

Focusing traps and re-collection tubes can contain multiple sorbents, for analysis of an extended range of analytes.



### 2. Trap desorption and outlet split:

Focusing trap rapidly heated (up to 100°C/s) in a reverse flow of carrier gas ('backflush' operation), to transfer the analytes to the GC column.



**Figure 1:** Two-stage direct thermal desorption.

Here, we use a TD100-xr™ automated thermal desorber (which automates the TD of up to 100 samples) coupled with a GC-MS to identify, quantify and characterise microplastic filtrates from bottled beverage samples.

## Experimental

Protocols for extraction of microplastics from the sample will be specific to the matrix under study – biota samples, for example, will require digestion steps prior to filtration while clear water samples are unlikely to require any specific sample pre-treatment. All sample types will undergo a filtration step to isolate the microplastic particles and, for TD-GC-MS analysis, from this point onwards, the sample preparation and analysis workflow is common.

Microplastics are collected onto quartz microfibre filters, which are then transferred to empty TD tubes, which are sealed with non-emitting, air-tight long-term storage caps. The filters remain in these tubes throughout storage and analysis. The tubes containing the filters are loaded into the TD autosampler and analysed via direct TD-GC-MS. Once the analysis is complete, the filter can be removed from the tube and disposed of and the tube re-used for another sample.

The protocol used for isolation and analysis of PET microplastics in this study is detailed below.

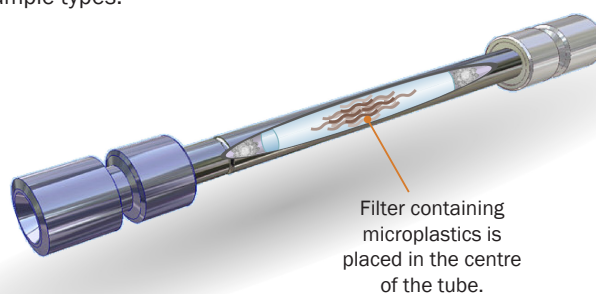
## Sample preparation

### Standards:

PET pellets (Sigma Aldrich) were ground into powder form using a ball mill with a ceramic ball. The resulting powder was weighed out onto 0.3 µm quartz microfibre 47 mm filter papers (QF1-047 CHM Lab) using a microbalance for weights between 0.02 and 0.8 mg. The filter paper was then folded and inserted midway into an empty TD tube before capping.

### Samples:

Liquid samples from bottled beverages were filtered through the 0.3 µm quartz microfibre filter papers. The filters were washed in multiple stages with hydrogen peroxide, acetone, and ultra-pure water to break down and remove any organic matter before drying them in an oven at 100°C for 30 minutes. The dried filters were folded and placed inside empty stainless-steel TD tubes, which were then capped before being stored prior to analysis (Figure 2). This sample preparation process is straightforward, takes less than an hour and can be applied to filters used for a wide range of sample types.



**Figure 2:** Prepared filtrates are placed into empty TD tubes for analysis.

**TD:**

Instrument: TD100-xr (Markes International)  
 Tubes: Empty stainless-steel tubes (CO-AXXX-0000)  
 Flow path: 200°C  
 Pre-purge: 1 min at 20 mL/min  
 Tube desorption: 320°C (12 min)  
 20 mL/min trap flow  
 60 mL/min split flow  
 Trap purge: 1.0 min at 50 mL/min  
 Focusing trap: 'Air toxics' (part no. U-T15ATA-2S)  
 Focusing trap low: -15°C  
 Focusing trap high: 300°C (3 min)  
 Trap heat rate: MAX  
 Outlet split: 30 mL/min

**GC:**

Column: DB-624™ 30 m × 0.25 mm × 1.4 µm  
 Carrier gas: Helium, constant flow  
 Column flow: 1.2 mL/min  
 Oven: 40°C (2 mins), 10°C/min to 60°C,  
 30°C/min to 250°C (7 min)

**MS:**

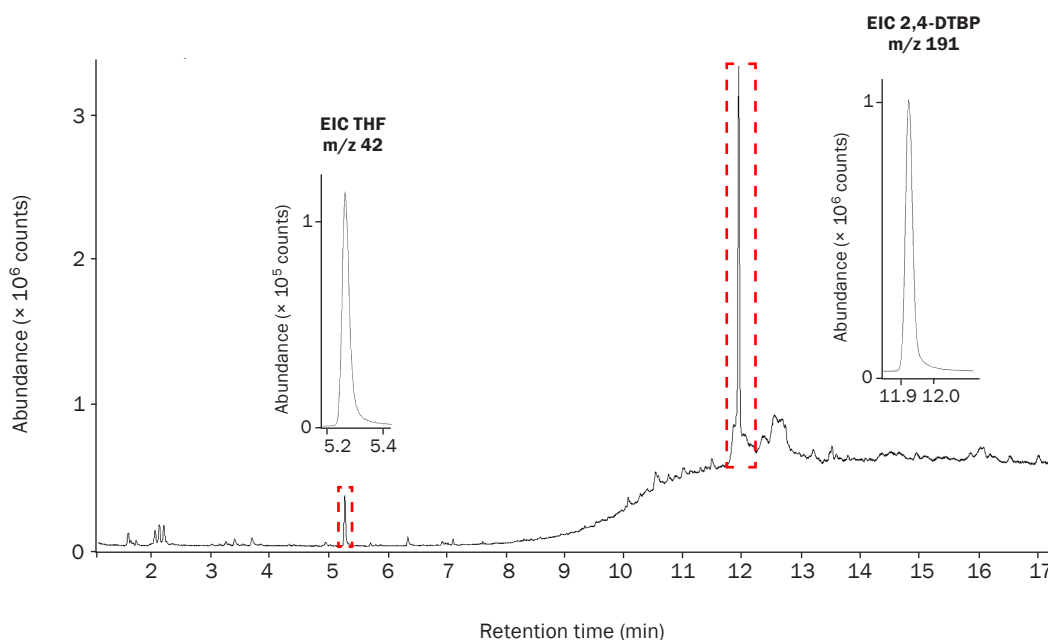
Source: 230°C  
 Transfer line: 230°C  
 Quadrupole: 150°C  
 Scan range: m/z 34–250

**Results and discussion**

To identify and measure target plastics by TD–GC–MS, VOCs released during desorption that can act as markers for these plastics must be identified and validated. VOCs can be present in environmental samples from a wide range of sources, so for confidence in results, it is important to validate multiple VOCs to act as a chemical fingerprint for the plastic under investigation. Validation of marker compounds for a wide range of plastics is ongoing and the work is subject to future publication. Here, we will present identification and quantitation of PET using two marker compounds.

**Quantitative analysis of PET**

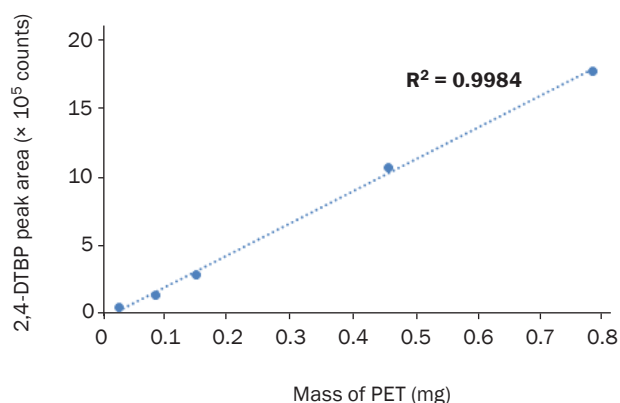
Preliminary studies identified 2,4-di-*tert*-butylphenol (2,4-DTBP) and tetrahydrofuran (THF) as the marker compounds for PET. 2,4-DTBP is the primary and quantitation marker, which means that the concentration of PET in a sample is measured using the amount of 2,4-DTBP detected. However, to identify PET in a sample, the confirmation marker THF must also be present. If THF is not detected, a negative result for PET is recorded. Figure 3 shows a typical total ion chromatogram of a PET standard with the marker compounds clearly identified.



**Figure 3:** Total ion chromatogram of the 0.8 mg PET standard analysed by direct TD–GC–MS. Insets are extracted ion chromatograms for quantitation marker 2,4-di-*tert*-butylphenol (m/z 191) and tetrahydrofuran (m/z 42).

### Calibration

To enable quantitative analysis of PET, a calibration was performed between 0.027 and 0.777 mg. Figure 4 shows excellent linear correlation, with  $R^2$  values  $>0.998$ , between the mass of PET and the peak area response for 2,4-DTBP, confirming that 2,4-DTBP can be used to quantify PET concentration.



**Figure 4:** Calibration curve of mass of PET against 2,4-di-tert-butylphenol peak area response over the range 0.027–0.777 mg.

### Background levels

It is important to confirm that sample preparation and analytical systems are free from any plastics that could contaminate the sample and lead to false positive results. There is a high risk of plastic contamination with microplastics analysis techniques in which samples undergo several sample preparation stages. The direct analysis of filters using TD avoids several manual handling steps so reduces the chance of contamination.

The analytical system in this study was verified as PET-free by analysis of an unused quartz fibre filter – no detectable levels of 2,4-DTBP or THF were found.

Milli-Q® ultrapure water (produced in the lab using a Milli-Q® Reference Water Purification System) was then processed through the sample preparation and analysis workflow and, again, no PET marker compounds were detected, confirming that the entire process is free from plastic contamination and appropriate for quantitative sample evaluation.

### Recovery validation

To validate the recovery of PET throughout the sample preparation and analysis workflow, a 2 L sample of verified PET-free water was spiked with 0.480 mg of PET and shaken vigorously. The spiked sample was then subjected to the entire workflow and analysed by TD–GC–MS. The concentration of PET was determined to be 220  $\mu\text{g/L}$ , demonstrating a recovery of  $>90\%$ .

### Measuring PET in bottled beverages

Bottles of still water purchased from a local convenience store were processed through the sample preparation and

analysis workflow to measure the concentrations of PET in the beverages. Detectable levels of 2,4-DTBP and THF were found in the water from Brand A, and the concentration of PET was quantified as 46  $\mu\text{g/L}$ . Neither 2,4-DTBP nor THF were detected in Brand B, indicating a negative result for the presence of PET. This could be due to a number of reasons such as different manufactures having different production processes or storage conditions, or they may use recycled materials. Carbonated water and a cola drink were also analysed. The results are shown in Table 1.

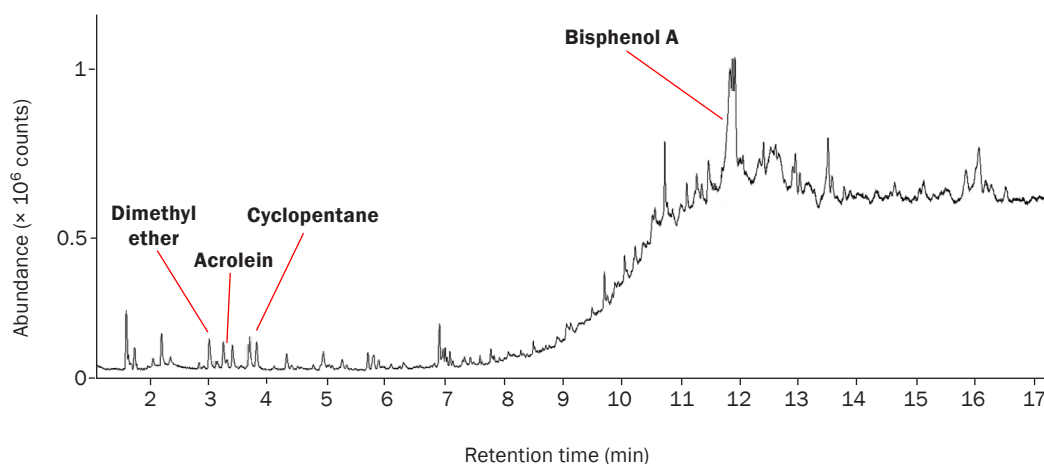
Sample type	Calculated concentration ( $\mu\text{g/L}$ )
Bottled water (still) (Brand A)	46.6
Bottled water (still) (Brand B)	n.d.
Bottled water (carbonated)	16.6
Bottled cola	22.1

**Table 1:** Concentrations of PET in bottled beverages calculated from 2,4-DTBP concentrations determined by TD–GC–MS..

### Characterising microplastics in real-world samples

Measuring the concentration of a specific plastic in a sample is only part of the story and the power of this analytical approach becomes apparent when we examine the VOC profiles and look beyond identification of the polymer. Unlike other chemical analysis techniques that use high temperatures to degrade polymers to enable identification of the plastic, TD uses relatively low temperatures. This not only enables identification of marker compounds, it also preserves other VOCs that could provide information about the source of the plastic and its journey through the environment and food chain.

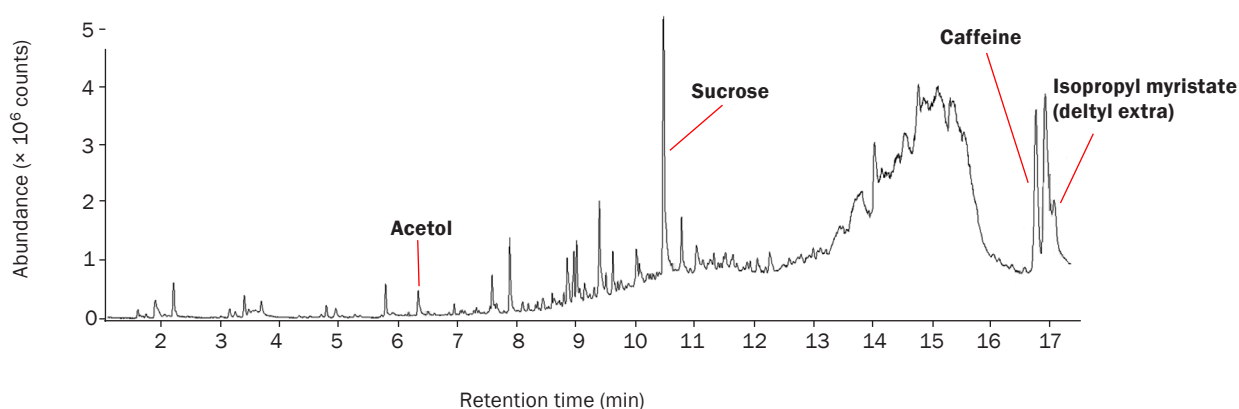
Several compounds reportedly used in plastics manufacturing were tentatively identified in the VOC profile from bottled water sample A (Figure 5) – dimethyl ether is used as a solvent in the manufacturing process,<sup>4</sup> acrolein is used to synthesise copolymers<sup>5</sup> and cyclopentane is utilised as a blowing agent<sup>6</sup> to harden plastics and resins. These were identified based on NIST spectral matching, all with forward match factors greater than 750. Bisphenol A (BPA) was also tentatively identified. BPA is often added during manufacturing to help harden plastics. Research suggests that BPA is an endocrine disruptor in humans and has the potential to cause harm via thyroid and reproductive hormones so its identification in microplastic samples could be important for toxicity assessments.<sup>7</sup>



**Figure 5:** Total ion chromatogram of TD-GC-MS analysis of microplastic filtrate from bottled water sample A. The highlighted compounds are associated with plastics manufacturing and could indicate the source of the plastic.

Contaminants absorbed by microplastic particles throughout their life cycle and the particles' journey through the environment is an emerging research area that is gaining significant interest. These contaminants could provide information on the source, original use and regional dispersion of microplastics found in environmental samples. As mentioned earlier, the low temperatures used with direct TD and its minimally destructive nature mean that the sample is not completely broken down, so the VOC profile containing the absorbed contaminants is preserved.

Figure 6 shows the TIC of the microplastics filtered from the cola sample. The chromatogram is more complex than those of the standards and the water samples, and confirms that PET microplastics retain contaminants from their environment, even after the sample preparation stages. A closer examination of the chromatogram reveals several compounds, including sucrose and caffeine, that link the microplastics to the cola drink that they were sampled from.



**Figure 6:** Total ion chromatogram of TD-GC-MS analysis of microplastic filtrate from a bottled cola sample. Caffeine, sucrose, acetol and detyl extra peaks are highlighted, which link the plastic filtrate to the cola drink it was sampled from.



## Conclusion

This application note has demonstrated the power of TD combined with GC–MS for the analysis of microplastics. Sample preparation is straightforward and takes significantly less time than many other analytical techniques. Simply placing the entire filter into an empty TD tube for analysis eliminates the inevitable losses and manual handling errors associated with transferring the microplastic from the filter to another vessel for analysis, a significant advantage over techniques such as pyrolysis. Analysis of the entire filter also avoids the challenge of obtaining a representative sample section from an inhomogeneous filtrate and provides a larger sample for analysis, making it a robust and highly sensitive analytical technique.

TD–GC–MS can be applied to filtrates from a wide range of sample types including water, soil, biota and air. Once the filtrate is collected, the analytical protocols are the same for any sample, which is ideal for laboratories with varying sample types and challenging matrices. In this study, the selection of 0.3 µm filters meant that all sizes of microplastic particles and even some nanoplastics (particles <1 µm) were captured. Many spectroscopic techniques suffer from particle size limitations so cannot cover the entire range of microplastics (let alone nanoplastics). TD–GC–MS extends the range of measurable particle sizes.

TD–GC–MS provides an automated process for microplastics analysis and automated data processing packages make the GC–MS data straightforward to interpret. Identification of 2,4-DTBP and THF as marker compounds for PET enabled quantitative analysis of PET concentrations (as µg/L) in bottled drinks. Full process blanks gave no detectable levels for these marker compounds and a test sample spiked with PET demonstrated >90% recovery.

Beyond measuring the target polymer, TD–GC–MS analysis simultaneously produces a VOC profile rich in information about the original plastic and the sample's journey through the environment. Identification of additives or colourants could enable identification of the source, use and possibly manufacturer, and aid toxicity profiling. Contaminants absorbed by microplastics, for example the caffeine in the microplastics from the cola in this study, can provide clues about the environments the microplastics have been exposed to.

Two additional features of Markes' TD instruments that will benefit microplastics analysis are automated re-collection and internal standard addition – both are widely adopted in materials analysis by TD. Re-collection, in which the split portion of a sample is automatically collected onto a sorbent-packed TD tube, allows a portion of the sample to be archived for further analysis under different conditions, maximising the information obtained from a single sample. This also avoids storing bulky samples. Internal standard addition transfers a precise aliquot of gas standard directly to the TD focusing trap for an automated, integral quality control and instrument performance measure in every analysis.

## References

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## Acknowledgements

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