

Protocols for the Material Library of Cladding Materials Part III: Sensitivity studies



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1 Background

This document aims to investigate measurement uncertainties in the testing methodology adopted in the “*Material Library for Cladding Materials*” project. The document investigates sensitivity of the results to testing methodology, sample preparation as well as sensitivity to the analysis procedure. The information presented here focuses on the materials which were most commonly encountered. It is important to note that some of the measurement uncertainties can be also dependent on the sample composition.

Given the high throughput requirements the sensitivity analysis cannot be performed for each individual material encountered during the project. Therefore, the results presented here should be interpreted only as examples that illustrate the approach followed when quantifying uncertainties. Furthermore, only the uncertainties deemed most complex or difficult to interpret are discussed here. Other uncertainties were assessed and were either considered to have little impact on the results or embedded in the standardised use of the equipment. As a result, the sensitivity analysis delivers a preferred methodology and an assessment of the potential errors (and their source) to be considered.

It is important to note, that the sole purpose of the screening protocol is to determine the uniqueness of the sample. It is not the purpose of the screening protocol to establish in a precise way the composition of the material. Precision has been subordinated to throughput to guarantee that the uniqueness of the material is defined but that materials can be tested in the fastest and most economic manner. This is essential, given the large number of products available in the market.

The information delivered by the screening protocol is sufficient to identify a material and guide the user towards a most effective use of the relevant flammability test data obtained by means of the detailed testing protocol.

2 Attenuated total reflectance Fourier transform infrared (ATR-FTIR)

2.1 Number of scans

Increasing the number of scans improves the signal to noise ratio and may prove useful for properly identify weak absorbance peaks, nevertheless it also increases the testing time. Thus, the choice of an adequate number of scans results form a balance between the desired quality of the results and the time taken to obtain the data.

Spectra of five different samples were taken and the number of scans was varied between 8, 16, 32, and 64 for each material (Figure 1). The first three samples – ACP02, ACP03 and ACP05 – all contain synthetic thermoplastic polymers. The absorbed IR spectra in all cases gives clear qualitative identification of all the relevant peaks. Of these, both ACP02 and ACP05 contain fire retardants and these can clearly be identified with even the lowest number of scans. The samples in these cases were thin slices taken from the side of the neat sample. The softness of these materials allows precise cutting and obtaining suitable samples for analysis using ATR-FTIR. A similar analysis was conducted for materials that allowed to obtain worse quality samples. These samples are OTH01 and OTH05 and are significantly more brittle. With brittle samples it is more difficult to obtain thin slices. Attempting to make a thin sample will end up breaking the sample into smaller flakes. The two results of OTH01 and OTH05 presented below were for samples which had broken into a powder/flake-like form. Applying pressure on the crystal allows a high amount of contact to ensure reasonable signal can be obtained. There is a significant amount of noise for both these samples, but nonetheless the peaks can be identified with a high certainty. The increase in the number of scans mostly has a small effect.

It is clear for the materials in the project that the number of scans does not result in significantly different results, and that an increase in the number of scans does not yield significant benefit. Nonetheless, the measurement time is still comparatively low compared to other test methods and so there is little to lose from an increased number of scans. Based on the above findings the number of scans was selected as 32. This represents a good compromise between high level of precision and measuring time.

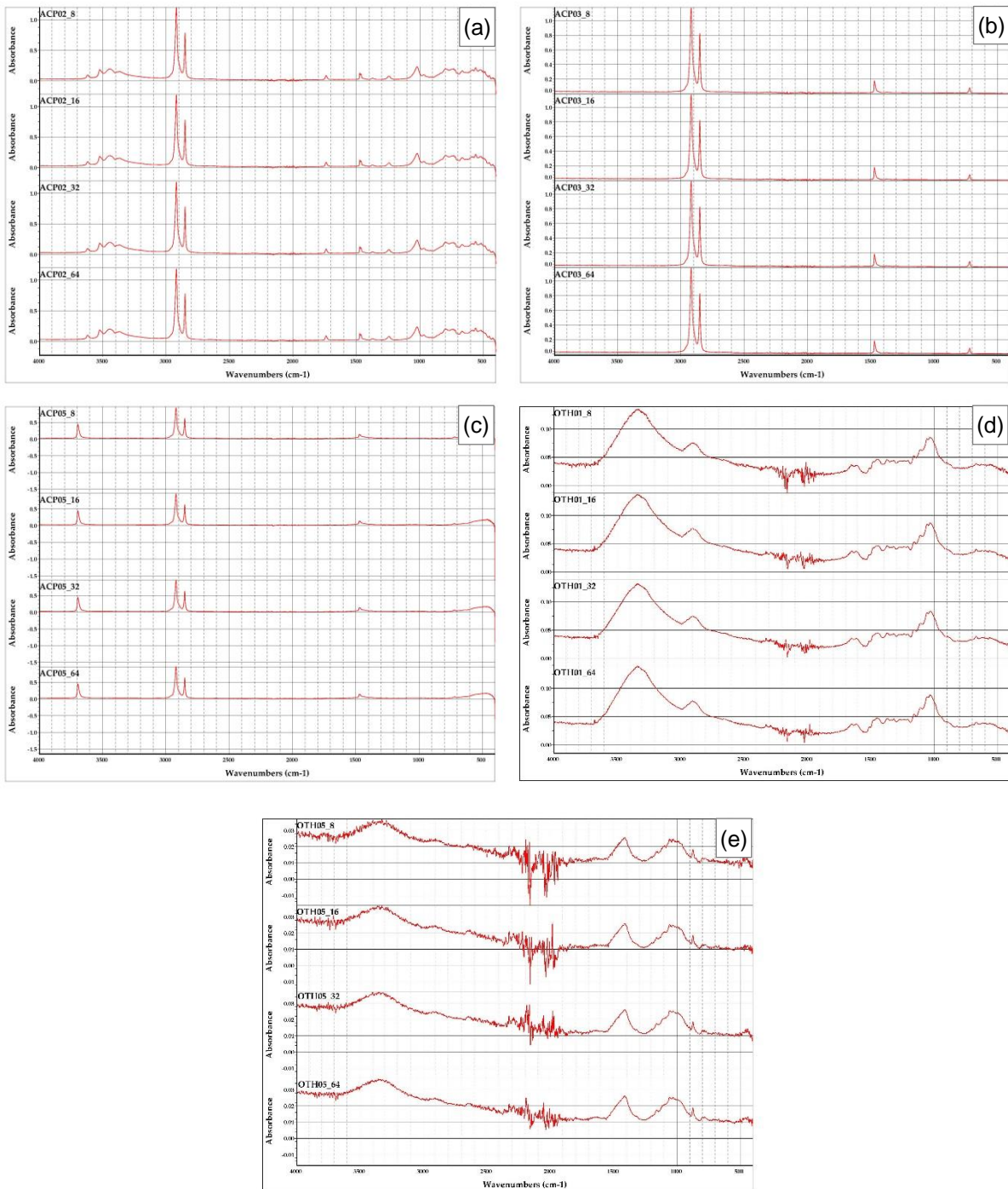


Figure 1 – Effect of number of scans 8, 16, 32 and 64 (from top spectrum to bottom in each plot) using ATR-FTIR for (a) ACP02 (b) ACP03 (c) ACP05 (d) OTH01 (e) OTH05. In each case, the tests were run on only a single location to better show effects.

2.2 Sample preparation

The penetration depth of the IR signal is very limited and consequently the information collected in ATR-FTIR typically stems from the first 15 μm of material from the sample surface. Provided the sample is significantly thicker than the penetration depth the sample thickness is not expected to be a critical parameter. However, for thick samples it becomes increasingly difficult to provide sufficient contact force between the sample and the crystal. Insufficient contact results in higher attenuation and a weaker signal.

A number of preparation methods were studied to find the optimal solution. These were as follows:

- Thin slice – a small (10–15 mm long, up to 4 mm wide and approx. 0.5–1.0 mm thick) slice was cut from the side of the sample. The thickness was the minimum that could be cut using a scalpel without failure of the material.
- Thick slice – a more substantial thickness slice from the side of the material. The same scalpel was used to cut a slice with dimensions approximately 10–15 mm long, 4 mm wide, and a thickness of 3 mm.
- Full sample – a complete 39 mm diameter disc was placed under the sensor with its full thickness, which is typically 4–6 mm for ACP samples and up to 25 mm for other samples. The metal skin on one side was removed for the ACP samples.
- Fused film – samples which were prepared for XRF analysis using cryogenic grinding and hot pressing.

Results of these four preparation methods for three samples is shown below in Figure 2. Each of the samples contain a thermoplastic polymer.

The full sample in each case shows the worst result with a reduced signal observed across the entire measurement range. This is expected to be due to the poor contact between the crystal and sample resulting in a higher attenuation of the signal. The dial used to apply pressure has little effect as the sample is insufficiently soft and too thick to be pressed against the crystal. This weaker signal makes it difficult to identify some of the smaller peaks, such as those corresponding to a low proportion of vinyl acetate in ACP07. Generally, the results are still sufficient to identify the components of each sample for these particular materials but key peaks could easily be missed.

Both the thin and thick slices have similar results and so will be discussed together. If the samples can compress and reduce in thickness when the pressure is applied, the results show that there is no noticeable effect of sample thickness. This suggests that both samples are in the correct thickness range, where sufficient contact pressure is obtained and where a sample thickness is retained that is larger than the penetration depth of the IR beam.

Having been cut neat, the surface is relatively flat and air voids are reduced by the application of pressure thus producing good quality spectra. The results in general are good, and the preparation method is both quick and easy. The cutting from the side of the sample enables a relatively homogeneous distribution to be analysed. Furthermore, the surface of the sample is maintained intact which can allow direct analysis using XRF if desired.

The final sample is the fused film which is produced for the optimal XRF analysis. This is the most expensive and time-consuming preparation method, but is nonetheless already used for the XRF. The results overall gave strong absorption peaks leading to clear identification of materials. This technique gives the clearest identification of peaks for ACP17, and the EVA component can clearly be seen. For each sample, the double peak around 1460 cm^{-1} is clearly and correctly identified with the fused film, where the other sample preparation techniques detect only a single peak. The sensitivity of the technique becomes more apparent for ACP07 where there is slightly worsened signal to noise ratio. This sensitivity is most likely due to the fact that the film is very thin and has the potential to be smaller than the penetration depth, which is in the order of microns.

The spectra of the fused film can therefore give the best results through use of the most expensive and time-consuming preparation method. Additionally, the application of the pressure to the crystal damages the surface of the sample which means that it cannot be re-analysed in XRF. For this reason, the near equal quality and reduced sensitivity of the thin slice is taken as the preferred sample preparation method. Whilst the results of the thick slice did not appear to vary, the thin slice is chosen to ensure that there is always good contact between the sample and crystal.

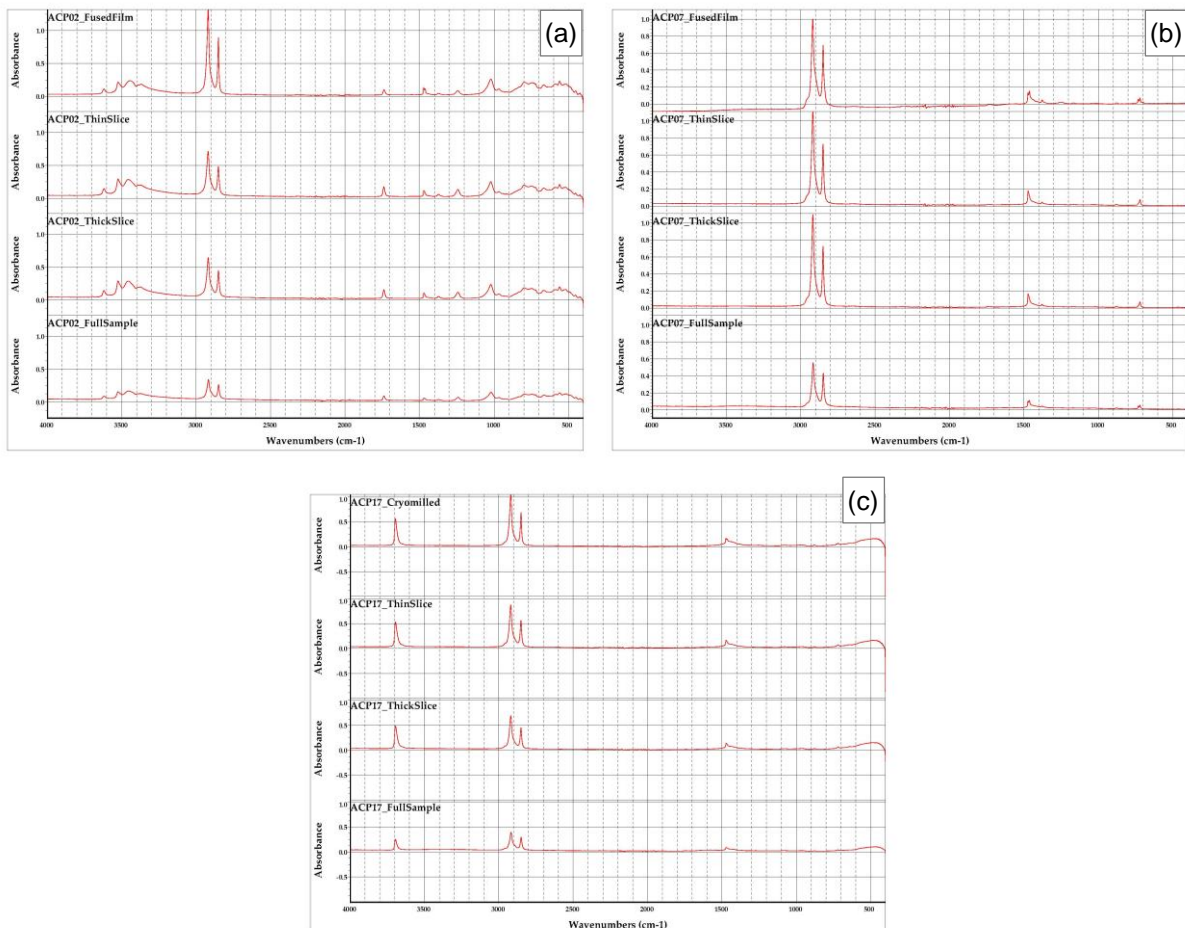


Figure 2 – Effect of sample location/type of sample for (a) ACP02 (b) ACP07 and (c) ACP17. Fused films were from cryomilling and hot pressing; slices were samples of varying thickness taken from the side of the specimen; and the full samples were tests on the full thickness of the disc. Tests each had 32 scans and had results averaged from three different locations.

3 Energy dispersive X-ray fluorescence (EDXRF)

The purpose of quantified chemical composition analysis is to provide a fingerprint of the material. Identification of the material has no bearing on the ultimate fire performance, and thus the chemical composition should only be used as a means to cross-reference the material to test results that establish the fire performance. Given the significant error in vertical flame spread, the tests that serve for assessment of propensity to vertical flame spread define the need for precision. The errors associated to these tests are so much larger than those used for screening that there is little gain for extremely accurate quantification of the chemical composition.

3.1 Background

Energy dispersive X-ray fluorescence (EDXRF) analysis is widely used across many industries for qualitative and quantitative compositional analysis. As discussed in “*Protocols for the Material Library of Cladding Materials – Part II: Sample Preparation and testing methodologies*”, the qualitative elemental composition identification is robust and the Bruker PUMA S2 equipment used has a measurement range of detecting elements from ppm to 100 % [1] i.e. where 100% is a completely pure element. However, when attempting to perform quantitative XRF analysis, there are a number of factors that can influence the quality of the results. The two major factors discussed here are the effect of sample preparation and compositional assumptions that need to be made during quantitative XRF analysis.

Despite its limitations, one of the advantages of XRF is that qualitative element analysis can be performed on most samples with minimal sample preparation (removal of the aluminium layer and, where present, removal of the adhesive layer). In combination with FTIR and TGA, the qualitative identification of the elemental composition provides an accurate indication of the uniqueness of a sample. This is what is necessary for screening purposes.

For screening testing, such as the testing performed as part of this study where over 1,000 samples were analysed, high sample throughput is critical. Sample preparation and time required for quantitative analysis are the limiting factors when it comes to throughput rate. Therefore the XRF approach was considered ideal.

For exact quantitative analysis, more care is required in the sample preparation and simple elemental analysis is no longer sufficient. It is important to note, that the purpose of this screening is not to provide the exact composition. The required precision is defined by the impact of composition of vertical flame spread. Given that many factors affect vertical flame spread, the quantification of vertical flame spread rates incurs a significant error, so the variability of the quantification of vertical flame spread rates is generally much larger than the potential errors induced when analysing XRF data.

Nevertheless, the following sections discuss the sensitivity of the XRF results to parameters relating to sample preparation and quantitative analysis assumptions.

3.2 Sample preparation method

Four sample preparation methods were investigated: sanded surface, milled surface, cryogenically grinded powder and fused film. Sanding the surface represents the simplest and quickest surface preparation method. Samples were sanded with a belt sanding machine with 120-grit sanding paper for 2–5 min. The aim of the sanding procedure was to remove the surface layer of the polymer material that was in contact with the aluminium surface. In order to expose a surface deeper within the sample, milling was employed using a 50 mm end-mill. The third procedure was cryogenic grinding of the sample. The final method corresponds to the cryogenically grinded sample followed by fusion of the powder into a film. This final method – cryogenic grinding into a powder then fusion into a film – is typically regarded as the “best-practice” in the XRF literature for samples of this type.

As shown in Figure 3 and Table 1, there is a noticeable difference between the quantitative results of the four sample preparation procedures. Sanded, milled and cryomilled powders clearly underestimate the quantity of

ATH (alumina trihydrate) fire retardant present in ACP11 by 15 %, 6 % and 10 % respectively. Furthermore, the spread of results – as represented by the standard deviation – is higher for each of these preparation methods when compared to the fused film. The exception is milling, which has a standard deviation (1.5 %) similar to the fused film (1.2 %). However, as seen in Table 2, all elements are qualitatively identified correctly, irrespective of the sample preparation procedure.

Fused film is recommended as the technique to provide definitive chemical composition quantification using XRF [2]. Milling, especially when paired with TGA, can give a consistent indicative value, capable of identifying the uniqueness of the sample. All ACP entries in the Material Library use the fused film to quantify the chemical composition.

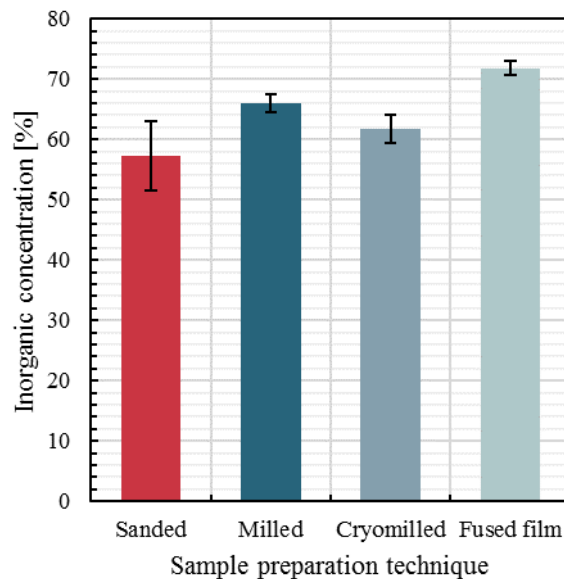


Figure 3 – Average and standard deviation for four ACP11 separate samples which were (i) sanded (ii) milled (iii) cryomilled into a powder, and then finally (iv) hot pressed into a fused film.

Table 1 – Composition of ACP11 samples using different sample preparation techniques. Values in the table are alumina trihydrate (AlO_3H_3) content measured in %.

	Sanded	Milled	Cryomilled (powder)	Fused film
Average	57.2	66.0	61.7	71.8
St. dev.	5.7	1.5	2.3	2.3

Table 2 – Summary of the elemental composition of samples (from above) with different preparation methods. All values in %.

	Sanded	Milled	Cryomilled (powder)	Fused film
Al	16.2	20.4	17.7	21.6
Mg	0.2	0.2	0.2	0.2
Si	0.1	0.1	0.1	0.1
Na	<0.1	0.2	0.2	0.2
K	0.1	0.1	0.1	0.0

3.3 Effect of depth on sample composition

The effect of sampling depth has been investigated to establish if there is variability within the sample. By removing polymer material in the thickness direction by milling and sanding different layers of material can be explored. The results presented in Figure 4 show that there was less than 5 % variation in the inorganic concentration detected with respect to sampling depth. Thus, there is a high degree of homogeneity of samples, even close to the aluminium skin. Extraction of samples for other testing methods (i.e. TGA and ATR-FTIR) should therefore be representative of the entire thickness of the ACP.

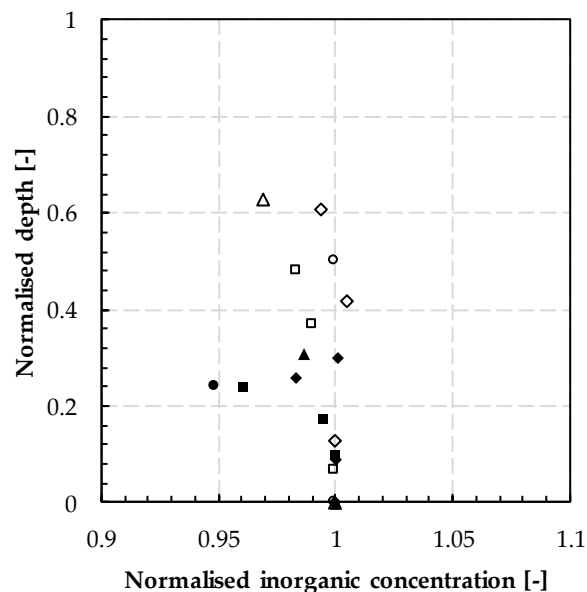


Figure 4 – The change of inorganic concentration within the depth of a sample. Hollow symbols are milled samples and filled symbols are sanded. A normalised depth of 0.5 represents halfway through the sample, and the normalised concentration is based on the composition measured at or near to the surface.

3.4 Perforated samples

In order to extract the cladding sample from the building façade, it is preferable to use a hole-saw with a pilot drill. The pilot drill centres the hole-saw during the drilling operation. As a consequence of this procedure, a hole exists in the centre of the sample. The presence of the hole does not affect TGA and FTIR analysis due to the fact that specimens are taken from the side of material. However, as the results show in Table 3, the presence of a 6.5 ± 0.3 mm diameter hole has a significant negative effect on the accuracy of the test results for quantitative XRF as this method analyses the complete surface. The samples had a total diameter of 39.7 ± 0.4 mm, but the visible testing area in the XRF sample holder was only 35.0 mm. For the majority of combinations tested, errors are in the range of 50% but in some cases the error was as high as 400%. The reason for these large errors can be explained by the fact that the X-rays that pass through the hole will not produce any X-ray fluorescence. The method used for quantitative XRF analysis assumes that the surface is complete, therefore interprets fluorescence emerging from the entire surface. In cases where this assumption is violated a large quantification error can occur.

These results clearly establish that a centre hole in the XRF samples is not permissible for quantitative analysis and as a consequence this sampling technique is not advised for sourcing cladding samples from buildings.

Table 3 – Comparison of element quantification in samples with and without a 5mm circular hole drilled through the centre. Data is normalised to inorganic concentration without a hole, i.e. 0.71 signifies a 29 % reduction in the element detection due to the presence of the hole.

	ACP01	ACP02	ACP03	ACP04	ACP30
Total inorganics [%]:	90	73	1	1	10
Ca	0.67		1.50	0.67	0.60
Mg	0.70	3.00	0		
Si	0.50		0.33		
Al	0.30	0.71	0		
S	1.00	0	0	0	
K	4.00				
Na	0			0.67	
Ti					0.78

3.5 ACPs with complex inorganic compositions

Compound quantification using XRF becomes increasingly difficult for samples which have complex inorganic compositions. This is due to a number of reasons:

- A large number of fire retardants or inorganic fillers are mined from naturally-occurring mineral deposits, and thus are often both impure and vary from region to region or deposit to deposit. This results in small amounts of minor compounds, and variance between every material.
- Quantification using XRF analysis is based on knowing in an *a priori* manner the correct compound, or compounds. If this is not correct, then the resulting quantification will not be accurate.
- Multiple compounds which contain the same base element cannot easily be differentiated using XRF. Similarly, ATR-FTIR and TGA can separate with difficulty overlapping signals not allowing for a clear differentiation and quantification between compounds.

3.5.1 Impurities

The majority of fire retardants/fillers are produced from naturally-occurring mineral deposits. Depending on the processing steps employed to obtain the fire retardant/filler, the purity can greatly vary. For example, nearly all alumina trihydrate is produced through the Bayer process and as a consequence typically has a high purity, in the order of 99 % for commercial grades. On the other hand, calcium carbonate can be produced either via precipitation or mined from calcium carbonate-containing rock such as limestone, chalk or dolomite. Calcium carbonate produced via precipitation has a very high purity (e.g. up to 99.995 %). However, when mined from calcium carbonate-containing rock (e.g. limestone) then the purity is far less, and varies greatly depending on the deposit location.

As a result, even seemingly relatively basic samples will in reality have complex compositions. Instead of a single portion of calcium carbonate, a sample may instead have numerous calcium-based compounds. This makes the identification of samples more difficult, as different materials may show after analysis concentrations of unknown inaccuracy due to these impurities. For the library, the analysis of the results simplifies the existing compounds to those identified in ATR-FTIR and supplemented by TGA. These commonly fall under alumina trihydrate, magnesium hydroxide, and calcium carbonate. The sensitivity and nature of this simplification is discussed in more detail in the following sections.

3.5.2 Errors

There are two compounding errors when the incorrect compound is used in the analysis:

- i. Errors due to the standard-less method having the incorrect compounds entered – the standard-less method calculates based on the shielding effect of the compounds entered. For example, by assuming that all calcium is calcium carbonate then the method adds the shielding effect of the CO_3 into the quantification for all calcium. When this is incorrect, this leads to an error quantifying the other elements in the sample because the shielding effect of the actual compound will be different.
- ii. Errors due to missing out other compounds sharing the same base element – the XRF analysis is not capable of distinguishing between different compounds with the same base element (e.g. MgO_2H_2 and MgCO_3 both share Mg as the element and thus cannot be differentiated). By assuming the incorrect compound then there will be a direct error in the quantification, and this leads to an inaccurate value for the total concentration of inorganics.

3.5.3 Sensitivity

The most suitable method to accurately quantify inorganic compounds is using X-Ray Diffraction (XRD). This is a technique similar to XRF which instead is used in crystalline materials to analyse their diffraction pattern. The intensity of the diffracted waves allows identification and quantification of compounds. However, XRD cannot precisely and consistently identify and quantify polymers by itself, and so additional techniques are required to achieve this.

To assess the sensitivity of XRF to complex and impure ACPs, indicative XRD testing of all unique samples contained in the Material Library was therefore performed using a Malvern Panalytical 600 W AERIS compact XRD Research-edition. This enables more accurate determination and quantification of the inorganics when paired with XRF and ATR-FTIR.

The results from the XRD analyses are shown in Table 4. The first two columns, labelled “XRF element analysis”, show the accurate and precise quantification of elements in the samples. The next two columns show the analysis as normally performed in the library, where a single compound is assumed for each single element. The actual expected identification is shown in the final two columns (“Joint XRF and XRD analysis”) where the quantification of the organic component in the XRF is supported by the quantification of inorganics in the XRD. Further iteration of the analyses between the XRF and XRD would allow the organic component to be re-calculated more accurately based on the true inorganic composition.

The impurities described previously in *Section 3.5.1 – Impurities* can be seen in the ACP samples in Table 4. The sample containing alumina trihydrate (ACP11) shows little to no change because the purity is very high (~99 %), as discussed earlier. This shows that the method outlined in this framework is able to accurately and precisely determine the composition of materials which contain highly pure components. The effect of the impurities can be seen in both ACP01 and ACP05 which likely originates from the rock deposits that they were mined from. For ACP05, quantification of the MgO_2H_2 is within 2.0 %. The assumption of the other small compounds is however shown to be inaccurate, and a much larger portion is assigned for various impurities. The result is most extreme in ACP01 due to the larger number of components, where the concentration of CaCO_3 is heavily overestimated and the XRD instead identifies the primary component as Ca_3SiO_5 . Further iteration between the XRD and XRF (i.e. inputting the correct compounds into XRF) would allow more accurate determination of the chemical composition.

Errors due to the incorrect compounds in the standard-less method – i.e. error (i) above – are expected to be small, in the region of 1–4 %. This is due to the fact that there is a limited impact that the similar compounds can have on the analysis. The major factor is that the elements must be correctly identified, and a reasonable compound must be input into the analysis.

In cases where there are elements which are not assigned to compounds – for example, Si and Ti in the initial XRF compound quantification in ACP05 have no compounds – then this results in a conservative outcome. The analysis shown using XRD is that these would have a greater mass (e.g. Si in the form of SiO_2 , Ca_3SiO_5 or $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) therefore the total inorganic concentration is underestimated in the Material Library, and the resulting organic portion is overestimated.

For error (ii) – the assumption of only one compound per element – there is the possibility of underestimating the inorganic concentration in some cases. This is due to the fact that the identified compounds using ATR-FTIR may not be the most conservative nor exactly matching the precise chemical composition. This is evident in ACP05 where the MgO_2H_2 content was overestimated by 2.0 %.

The purpose of the screening protocol in the Material Library is to identify the uniqueness of each material to enable cross-referencing with the detailed testing protocol, as described in detail in “*Protocols of the Material Library of Cladding Materials – Part IV: Use and interpretation*” [3]. The use of XRD allows more accurate quantification of inorganic compounds but is only valid for crystalline materials. Therefore the decision to use XRF was due to the fact that it can analyse a wider range of cladding samples.

Table 4 – Inorganic composition for ACP01, ACP05 and ACP11. The XRF compound analysis assumes that the elements Ca, Al and Mg correspond to CaCO_3 , AlO_3H_3 and MgO_2H_2 respectively. The XRD analysis relies on the quantification of total inorganic content by the XRF.

XRF elemental analysis		XRF compound analysis		Joint XRF and XRD analysis	
<i>ACP01</i>					
Ca	37.5	CaCO_3	51.1	Ca_3SiO_5	29.2
Al	7.8	AlO_3H_3	19.6	AlO_3H_3	28.8
Mg	5.7	MgO_2H_2	13.2	CaCO_3	18.4
Si	4.7	SiO_2	7.9	MgO_2H_2	10.1
S	0.8	S	0.6	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	5.2
				$\text{CaMg}(\text{CO}_3)_2$	0.8
				SiO_2	0.7
<i>ACP05</i>					
Mg	21.2	MgO_2H_2	57.8	MgO_2H_2	55.8
Ca	5.0	CaCO_3	7.2	MgCO_3	5.9
Si	1.4	Si	1.0	$\text{CaMg}(\text{CO}_3)_2$	1.9
Ti	1.2	Ti	0.6	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$	0.5
				CaCO_3	0.4
<i>ACP11</i>					
Al	22.0	$\text{Al}(\text{OH})_3$	71.8	$\text{Al}(\text{OH})_3$	71.8
Mg	0.3	Mg	0.5	Al_2O_3	0.7
Si	0.2	Na	0.1		
Ca	0.1	Si	0.1		

4 Thermogravimetric analysis (TGA)

4.1 Effect of sample size and sample mass

It is well understood that the sample quantity and size affect the results of the TGA analysis due to differences in the thermal inertia and exposed surface area. In order to explore the sensitivity to these two parameters (sample quantity and size), a sensitivity study was performed with cladding shavings of differing size and sample mass. Three grades of shavings were prepared (see Figure 5):

1. Fine particles with a length of 0.5–3 mm
2. Medium sized shavings with a length of 3–5 mm
3. Large shavings with a length of 5–10 mm

Each sample grade was tested in 5 mg and 15 mg quantities. For this analysis, ACP11 was used as this material shows multiple degradation reactions.



Figure 5 – Different sample sizes – small (left), medium (centre) and large particles (right).

As expected, there is a correlation between TGA results and the sample size and tested quantity (Figure 6 and Figure 7). The finer particles exhibit marginally earlier onset of the degradation and a higher mass loss. The sensitivity to these parameters is however small. The total residue percentage varied less than 1.7 % and the peak position of the degradation reaction (peak DTG) varied less than 3.5 % from average of all samples tested. Appendix A-1 summarizes the tabulated test results and deviations. One can conclude that the sensitivity to sample size and quantity is relatively small. In order to obtain conservative results, it is advisable to opt for small particle size and small sample quantity.

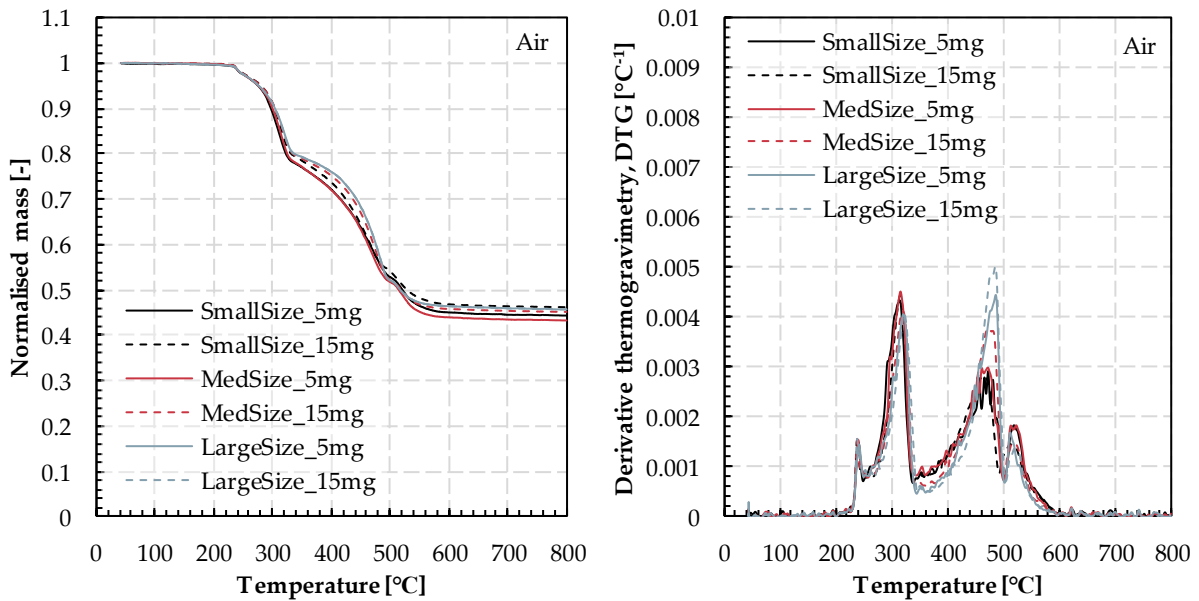


Figure 6 – Thermogravimetry (left) and associated derivative (right) of ACP11 in an air environment with a heating rate of 20 °C min⁻¹. Small particle samples (black), medium size (red), and large size (blue/gray) are shown for two sample weights: 5 mg (solid lines) and 15 mg (dashed lines).

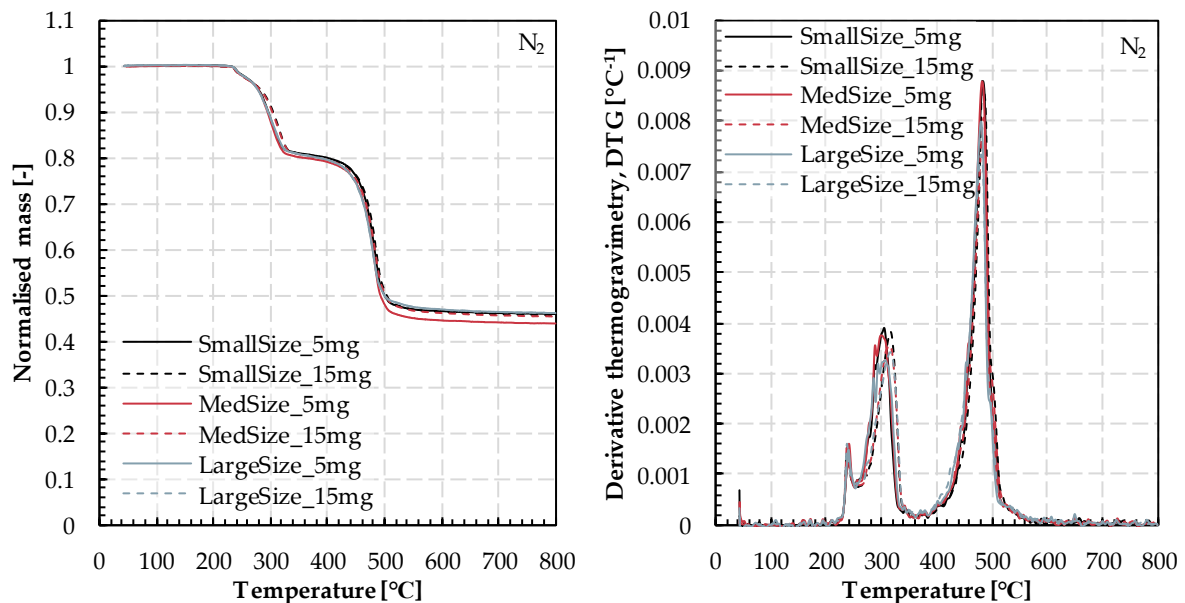


Figure 7 – Thermogravimetry (left) and associated derivative (right) of ACP11 in a nitrogen environment with a heating rate of 20 °C min⁻¹. Small particle samples (black), medium size (red), and large size (blue/gray) are shown for two sample weights: 5 mg (solid lines) and 15 mg (dashed lines).

4.2 Location of sampling

In order to preserve the screening samples for the XRF analysis, TGA samples were extracted from the edge of the sample. Repeats were performed for all TGA samples and across the more than 2,000 TGA tests performed as part of the Material Library development there was no particular sensitivity to the sample location observed.

4.3 Back calculation of material composition

If the degradation reaction of a given fire retardant is known, then the quantity of fire retardant can be back-calculated from the TGA under the following assumptions:

- The fire retardant follows the assumed reaction scheme;
- The char yield of the polymer is known or the polymer matrix does not produce any char;
- The fire retardant is pure and has the chemical composition assumed by the reaction scheme; and
- There are no interactions between the polymer and fire retardant or other additives present in the sample material.

It is worth noting that the above conditions are not always met. Whereas the char yield of the two most commonly encountered polymers in ACPs, polyethylene and polyethylene-vinyl acetate (EVA), is zero, the purity of the filler or fire retardants is not always sufficient to allow back-calculation. Table 4 previously showed the composition of specific samples determined with X-ray diffraction analysis (XRD). This analysis showed that alumina trihydrate fire retardant typically has a very high purity. Magnesium hydroxide and particularly calcium carbonate-based fire retardants are however less pure and hence back-calculation is not always possible. The same is true for cases where a sample contains multiple fire retardants. For example, magnesium hydroxide is commonly seen in combination with calcium carbonate.

The reaction schemes for the three most commonly used fire retardants and inorganic fillers are shown below in Table 5 which are used as part of the back-calculation. As shown in Table 6, the post-pyrolysis residue of aluminium trihydrate determined via TGA matches the predicted value very well. These results clearly demonstrate that for alumina trihydrate-containing samples the back-calculation provides an accurate way of determining the retardant concentration. A maximum error of 3.5 % between the back-calculated value and the value determined by XRF was observed. In the case of magnesium hydroxide, the measured residue in TGA and the expected residue based on the reaction scheme already differ by 4 %. This error also translates into a large error when attempting the back-calculation for sample ACP05. The retardant quantity determined by XRF and TGA back-calculation differ by 6.7 %. Note that the calculation in this case for ACP05 assumes that the residue in the TGA was only magnesium hydroxide and the calcium carbonate was not considered. This is an extreme case to show the maximum expected deviation.

Table 5 – Reaction scheme of common inorganic additives.

(a) Alumina trihydrate

Reaction:	2 Al(OH) ₃	→	Al ₂ O ₃	+	3 H ₂ O
Mass [g]	156		102	+	54
Ratio [-]	1.000		0.654	+	0.346

(b) Magnesium hydroxide

Reaction:	Mg(OH) ₂	→	MgO	+	H ₂ O
Mass [g]	58.3		10.3	+	18
Ratio [-]	1.000		0.691	+	0.309

(c) Calcium carbonate

Reaction:	CaCO ₃	→	CaO	+	CO ₂
Mass [g]	100.1		56.1	+	44
Ratio [-]	1.000		0.560	+	0.440

Table 6 – Comparison of composition quantification between EDXRF and a back-calculation using the TGA.

Library ID-sample number	Residue in TGA [%]	Inorganics _{TGA} [%]	Inorganics _{XRF} [%]	Change [%]
<i>Alumina trihydrate-based samples</i>				
Alumina trihydrate (>99% purity)	65.0	65.4	-	-0.4
ACP11-9	45.8	70.1	73.5	-3.4
ACP11-10	45.8	70.0	73.5	-3.5
ACP11-11	46.1	70.5	73.5	-3.0
ACP11-12	46.7	71.4	73.5	-2.1
ACP11-13	47.5	72.6	73.5	-0.9
ACP02	46.2	70.6	72.6	-2.0
<i>Magnesium hydroxide-based samples</i>				
Magnesium hydroxide (unspecified purity)	65.1	69.1	-	-4.0
ACP05	40.7	60.8	67.5	-6.7

4.4 Selection of maximum temperature

TGA tests were performed from 50 to 800 °C. The 800 °C cut-off was determined from initial screening tests where TGA was performed to a temperature of 1200 °C. As highlighted in Figure 8 and Figure 9, the mass loss above 800 °C is small. The mass loss between 800–1200 °C for ACP01 was 0.30% in air and 1.25% in nitrogen. For ACP03, the mass loss was close to 0 % in both air and nitrogen for the same temperature range (the mass loss was less than the measurement error). Consequently, terminating the TGA test at 800 °C

provides a good compromise between accurately determining the final mass loss and the time required for the test.

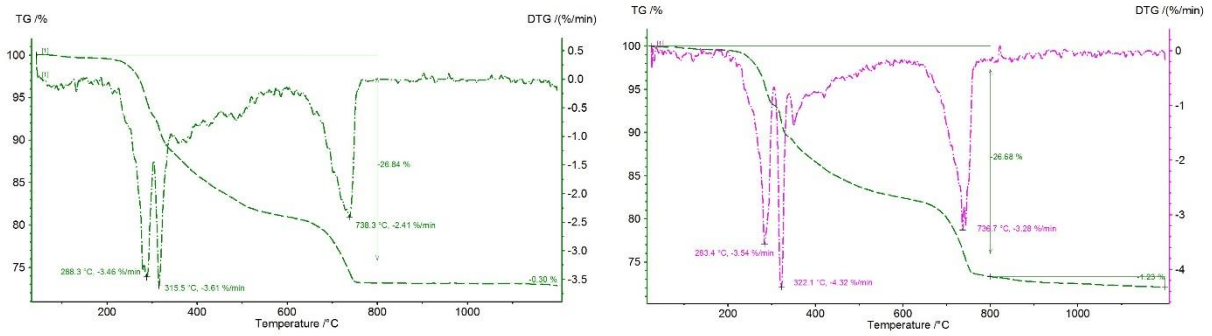


Figure 8 – Experiments of ACP01 in air (left) and nitrogen (right) atmospheres up to a temperature of 1200 °C with a heating rate of 20 °C min⁻¹.

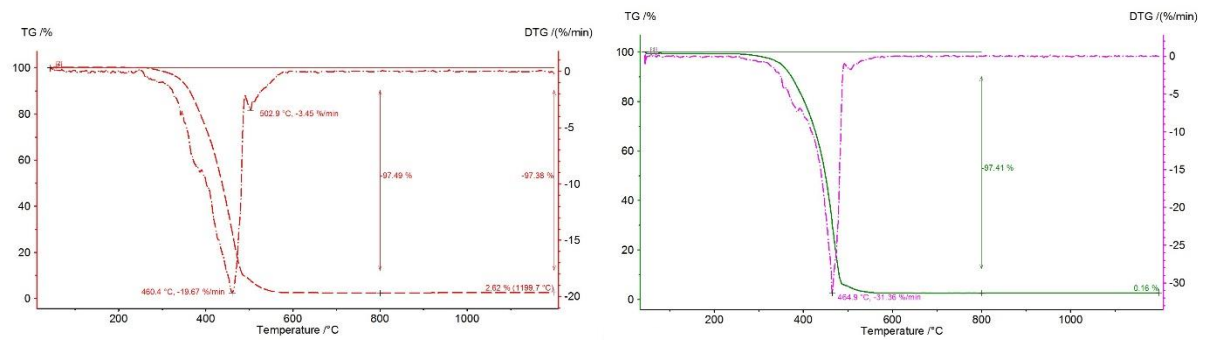


Figure 9 – Experiments of ACP03 in air (left) and nitrogen (right) atmospheres up to a temperature of 1200 °C with a heating rate of 20 °C min⁻¹.

5 References

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6 Acknowledgements

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A-1 Appendix – TGA data for varying particle size and mass

Table A.1 – Data from TGA in air for the varying particle sizes and sample masses.

Size	Mass	Residue	Deviation from average	1st Peak				2nd Peak				3rd Peak				4th Peak			
				Temp	Deviation from average	DTG	Deviation from average	Temp	Deviation from average	DTG	Deviation from average	Temp	Deviation from average	DTG	Deviation from average	Temp	Deviation from average	DTG	Deviation from average
-	mg	%	%	°C	°C	°C ⁻¹	°C ⁻¹	°C	°C	°C ⁻¹	°C ⁻¹	°C	°C	°C ⁻¹	°C ⁻¹	°C	°C	°C ⁻¹	°C ⁻¹
Large	5	45.7	0.8	241.1	2.0	0.0014	-0.0001	320.6	2.9	0.0041	-0.0002	486.0	10.5	0.0044	0.0008	512.0	-5.4	0.0017	0.0001
Large	15	45.0	0.0	237.9	-1.2	0.0016	0.0000	321.8	4.1	0.0041	-0.0002	485.3	9.8	0.0050	0.0014	519.6	2.2	0.0014	-0.0002
Medium	5	43.3	-1.7	239.8	0.7	0.0015	0.0000	315.4	-2.4	0.0045	0.0003	471.7	-3.8	0.0030	-0.0007	522.5	5.1	0.0018	0.0002
Medium	15	45.2	0.2	237.9	-1.2	0.0016	0.0000	319.7	1.9	0.0041	-0.0001	473.5	-2.0	0.0038	0.0001	519.8	2.4	0.0015	-0.0001
Small	5	44.4	-0.6	240.3	1.2	0.0015	0.0000	314.2	-3.6	0.0043	0.0001	472.4	-3.1	0.0029	-0.0007	518.7	1.3	0.0018	0.0002
Small	15	46.2	1.3	237.6	-1.5	0.0015	0.0000	314.8	-2.9	0.0044	0.0002	464.0	-11.5	0.0028	-0.0008	511.6	-5.8	0.0015	-0.0002

Table A.2 – Data from TGA in nitrogen for the varying particle sizes and sample masses.

Size	Mass	Residue	Deviation from average	1st Peak				2nd Peak				3rd Peak			
				Temp	Deviation from average	DTG	Deviation from average	Temp	Deviation from average	DTG	Deviation from average	Temp	Deviation from average	DTG	Deviation from average
-	mg	%	%	°C	°C	°C ⁻¹	°C ⁻¹	°C	°C	°C ⁻¹	°C ⁻¹	°C	°C	°C ⁻¹	°C ⁻¹
Large	5	46.1	0.7	240.4	1.1	0.0015	-0.0001	306.8	-2.9	0.0033	-0.0004	480.2	-2.3	0.0080	-0.0003
Large	15	45.4	0.0	237.8	-1.5	0.0016	0.0001	316.2	6.5	0.0034	-0.0002	480.7	-1.8	0.0073	-0.0010
Medium	5	43.9	-1.5	241.4	2.1	0.0016	0.0001	299.3	-10.4	0.0038	0.0001	482.4	-0.1	0.0088	0.0005
Medium	15	45.4	0.0	237.9	-1.4	0.0016	0.0000	314.3	4.6	0.0036	-0.0001	485.1	2.6	0.0081	-0.0002
Small	5	45.9	0.5	240.6	1.3	0.0015	-0.0001	305.0	-4.7	0.0039	0.0003	483.8	1.3	0.0088	0.0005
Small	15	45.7	0.3	237.7	-1.6	0.0015	0.0000	316.7	7.0	0.0038	0.0002	482.6	0.1	0.0088	0.0005



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