

# Molecular Fingerprint of Condensate Residues in the Soldering Process - Detailed FT-IR Spectroscopic Analyses and Identification of Reaction Partners

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## ABSTRACT

During dynamic times, electronics production faces global supply shortages, cost pressures and a higher development challenge. These challenges result in higher supplier and raw material change, higher quality deviations, higher waste levels and an additional environmental impact. Particularly in the PCB manufacturing industry, where volatile components outgas from the PCB substrate, solder paste and components at high temperatures during the soldering process and condense in the soldering machines as a toxic residue, the focus must be on the subject of condensate residues. Although some of this condensate residue is collected in the soldering machines during production, a certain amount of the condensate escapes and contaminates our environment as toxic hazardous waste.

It is therefore important to identify what the condensate consists of, what are its formation mechanisms and where it could be meaningfully and efficiently removed or at least inhibited in its formation. In order to increase the sustainability and environmental friendliness of electronics production, the topic of condensate formation, polymerization and crosslinking was theoretically investigated in detail in a previous paper: "Detailed Study of Condensate Residues - Analysis of the Responsible Reaction Partners as well as Reasons for Condensate Polymerization and Growth of Crystalline Structures in the Soldering Process". Furthermore, potential reaction mechanisms were investigated and substances were analyzed which may be involved in chemical polymerization and crosslinking reactions and thus in the formation of condensate residues. This theoretical work is the background for the next step - condensate analyses on the molecular level, identification of its components and verification of the chemical reaction processes.

Key words: soldering, soldering process, reflow, condensate residue, FT-IR, spectroscopy, PCB, electronics.

## INTRODUCTION

This work focuses on condensate analyses from electronics manufacturing. For this reason, a wide range of condensate samples were taken from different process zones of reflow soldering systems and were analyzed using FT-IR spectrometry. These analyses provide deep insights not only into the outgassing process but also into the reaction process of the different compounds in the condensate residue. Different process zones of a reflow soldering system have

different temperature ranges where specific molecular components from the solder paste, solder resist and PCB substrate outgas, condense and react with each other (Figure 1 and 2). Like a fingerprint, FT-IR spectroscopy can be used to identify the composition of the condensate residue in the respective temperature range. Previous deviations in production processes such as an incompletely cross-linked solder mask due to the presence of oxygen during their manufacturing, leave their traces in the condensate residue as well as the hardener from the PCB substrate, which is present in excess.

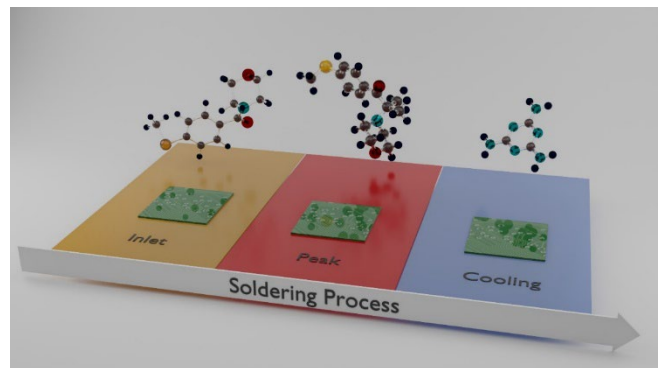


Figure 1. Outgassing molecules in different zones of the reflow machine during the soldering process

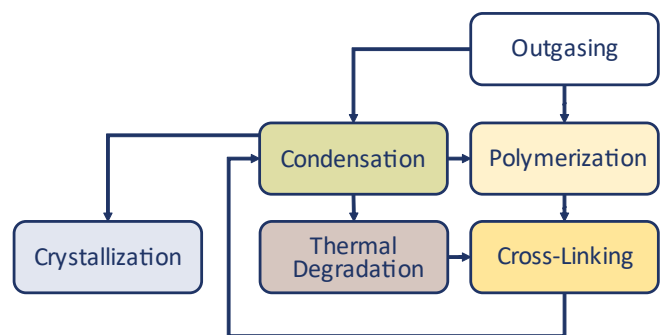


Figure 2. Process of condensate formation and crystallization

The spectroscopic analyses of condensate residues confirm the theoretical work of detailed study of condensate residues<sup>[1]</sup> and help electronics manufacturing industry to inhibit condensate formation or to remove specific gaseous substances from the process for further chemical polymerization and crosslinking reactions by adjusting the temperature outside the soldering process. The growth of

crystalline formations can also be minimized, when the responsible substance has been identified, by extracting the reaction partners or by changing the temperature range. This can extend maintenance cycles, reduce the formation of substances that are harmful to health and the environment, and increase the productivity of soldering systems.

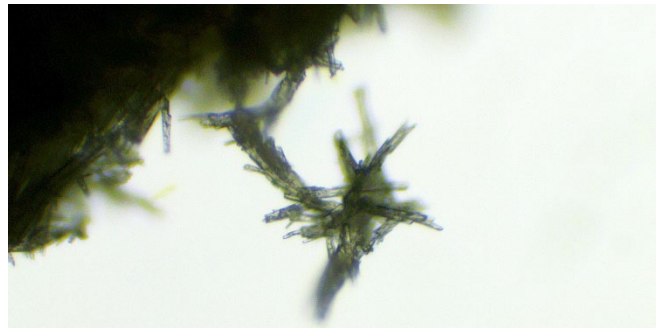
### ANALYSES OF CONDENSATE RESIDUES

#### Procedure, Extraction of Samples and Analysis

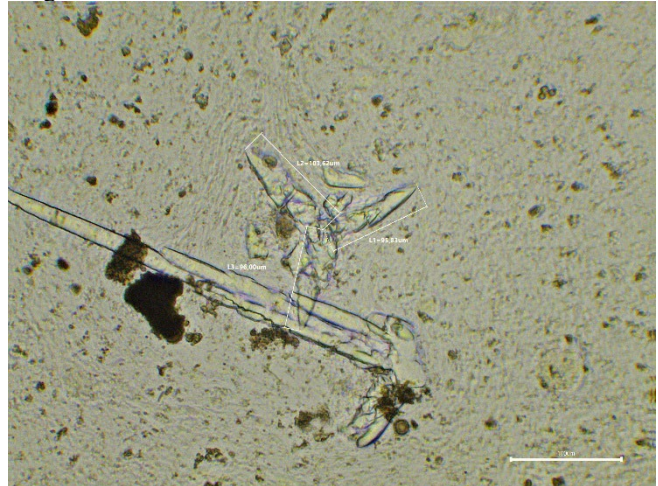
For the FT-IR spectroscopic analyses, samples of the condensate residue were taken from different areas of a reflow soldering machine during the maintenance interval. The samples were collected from the inlet area, the peak area and the cooling area. The goal is to identify the substances that outgas from the PCB, solder resist, components, and flux at different temperatures. Possible changes in comparison to the spectrum of the pure substance, which indicate a thermal or chemical degradation, polymerization and crosslinking reaction, also will be analyzed in more detail here.

Condensate residue samples taken for FT-IR analyses were sealed airtight in 15 ml laboratory vials immediately after collection and not opened until analysis to avoid influence of humidity and oxidation by oxygen. The molecular fingerprint was determined using a spectrometer from Bruker, type Tensor 27. For the FT-IR analyses, the respective condensate sample has been removed from the airtight vial and placed on the measuring cell (Pike Miracle, ZnSe optics) of the FT-IR spectrometer for analysis.

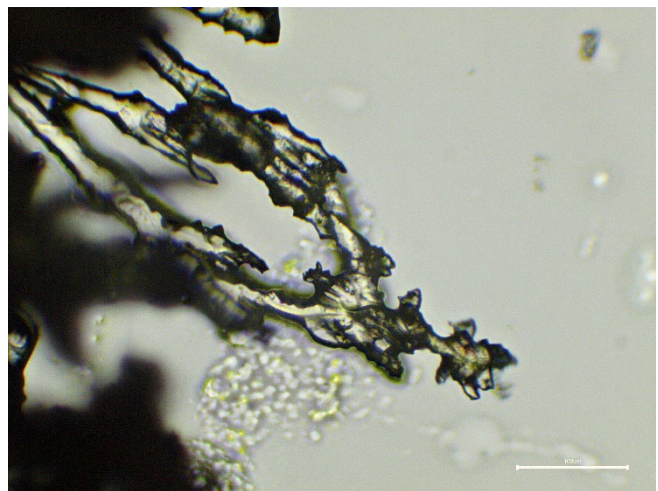
In addition to the FT-IR analyses, microscopic analyses were also performed on the condensate residues. All condensate samples had a viscous consistency with solid particles and partially crystalline structures. The microscopic images were performed in transmitted light so that possible conclusions could be drawn about the crystalline structure in the condensate samples. Microscopic images at a 40x (Figure 3) and 100x magnification (Figures 4 and 5) show numerous smaller particles and, particularly, crystalline structures in the condensate residue. Remarkable here are crystals which grow with three equal edge lengths and have an angle between the single edges of about  $120^\circ$  (Figure 4). There are also crystalline structures which have acicular and branching structures (Figure 5). The size of the individual crystalline structures is between  $56\mu\text{m}$ - $100\mu\text{m}$ .



**Figure 3.** Crystalline Condensate Residue, 40x Magnification



**Figure 4.** Crystalline Condensate Residue with Three Equal Edges

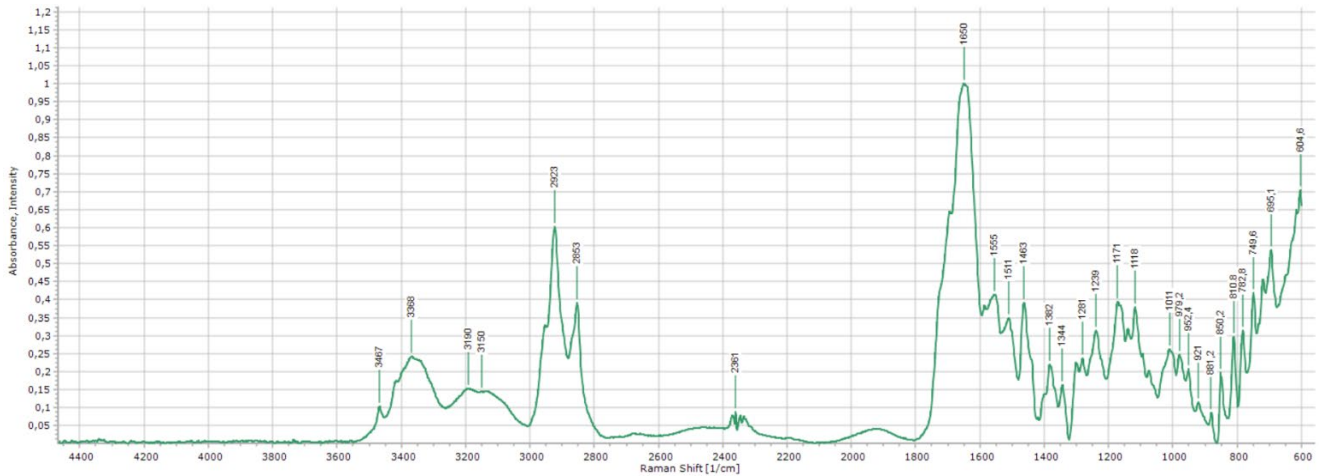


**Figure 5.** Crystalline Condensate Residue with Branching Structure

## RESULTS DISCUSSION

The spectra of the condensate residues are significantly different from each other. This clearly shows the presence of different chemical compounds, although the same process gas atmosphere was extracted from the soldering process,

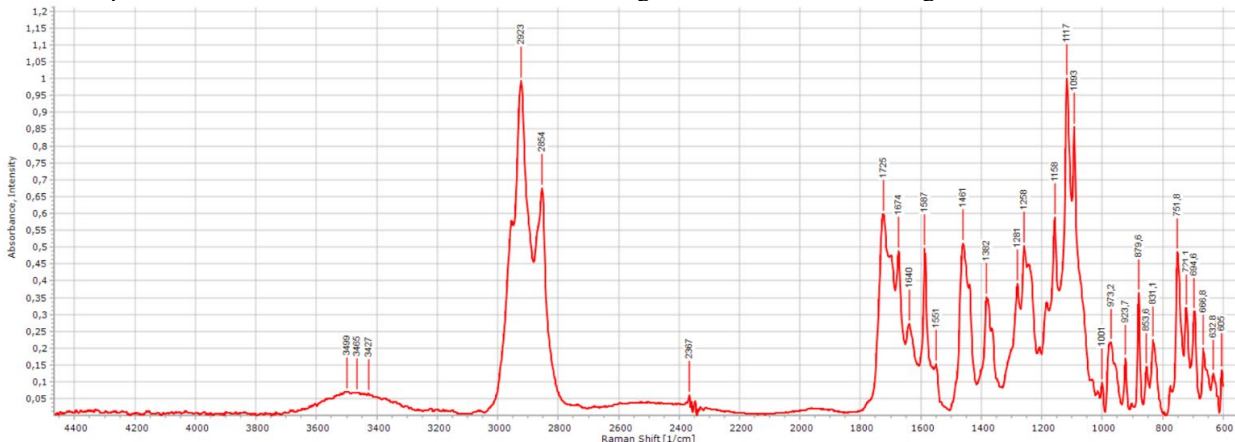
cleaned and then returned to the process. Figure 6 shows the spectrum of the condensate residue from the inlet area of the reflow soldering system. The prominent peaks have been marked accordingly.



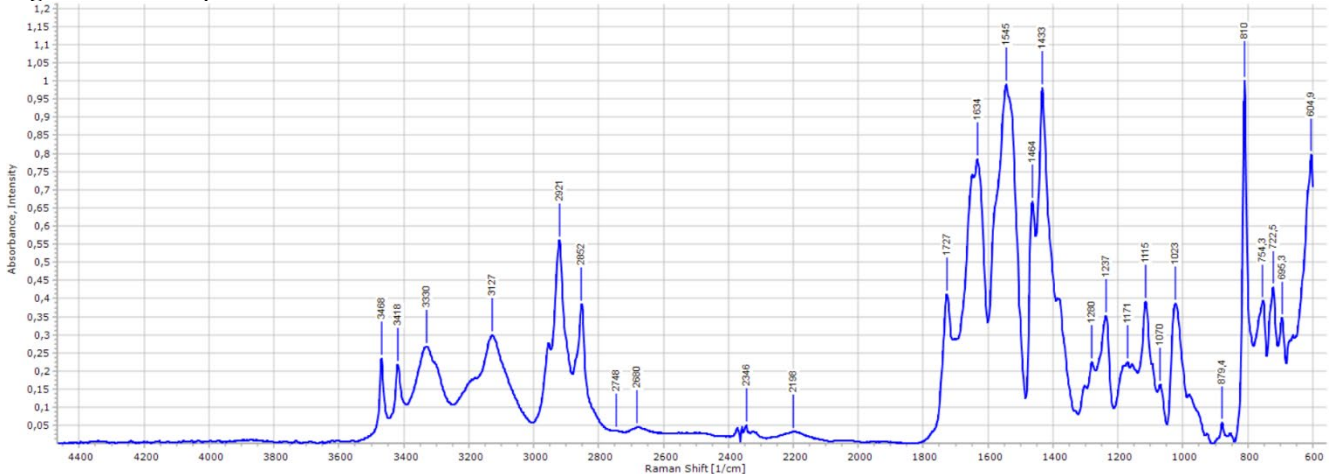
**Figure 6.** FT-IR Spectrum of the Condensate Residue from the Inlet Area

The spectrum of the condensate residue from the peak zone is shown in Figure 7. The spectrum is significantly different from the spectra of the condensate from the inlet and cooling

zones in the wavenumber range from  $3600\text{cm}^{-1}$  to  $3000\text{cm}^{-1}$ . Only a weak peak at  $3465\text{cm}^{-1}$  matches the other spectra in this wavenumber range.



**Figure 7.** FT-IR Spectrum of the Condensate Residue from the Peak Area



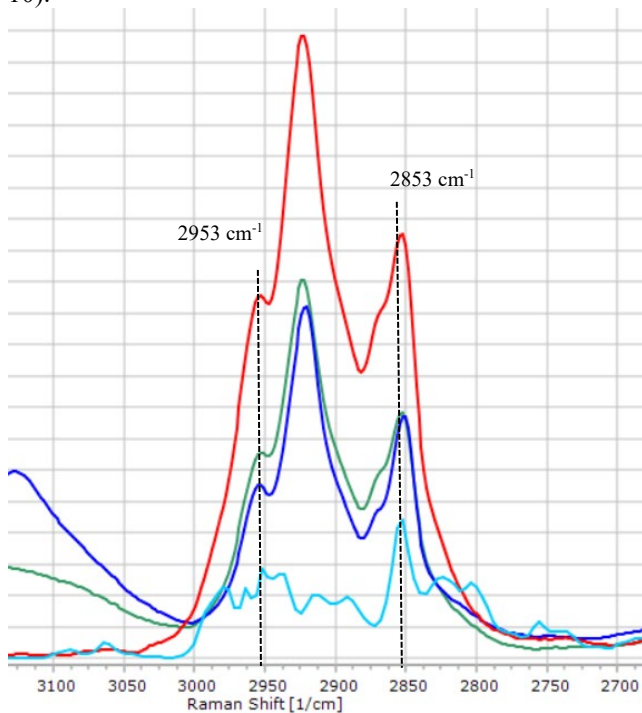
**Figure 8.** FT-IR Spectrum of the Condensate Residue from the Cooling Area

Figure 8 shows the spectrum of the condensate residue from the cooling zone. It shows a similarity in spectrum with the condensate residue from the inlet zone of the reflow machine.

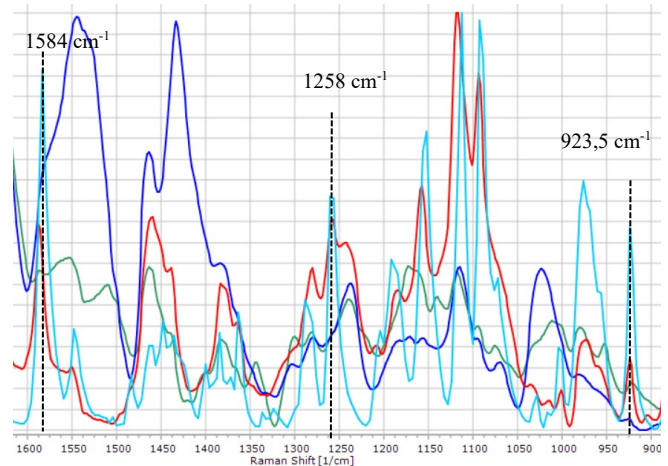
In all condensate samples peaks related to the =CH<sub>2</sub> vibration are present [2]. These are located at 2953 cm<sup>-1</sup>, 2923 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>. These are in particular valence vibrations. Also, =CH<sub>2</sub> deformation vibrations appear at 1463 cm<sup>-1</sup> and 1439 cm<sup>-1</sup> as well as the =CH<sub>2</sub> rocking vibrations at 722 cm<sup>-1</sup>.

### Crystalline Condensate Residue - 2-methyl-4'-(methylthio)-2-morpholinopropiophenone

The photoinitiator 2-methyl-4'-(methylthio)-2-morpholinopropiophenone was identified as the origin of the crystalline condensate residue observed under the microscope (Figure 3) by database search. Condensate samples from the inlet area, peak area and cooling area show correlation with a significant molecular signature from this substance. Since its melting temperature is at 75°C, it is most probably already exposed in the inlet area of the reflow soldering machine and distributed through the soldering atmosphere in the peak and cooling zones. The highest correlation with 2-methyl-4'-(methylthio)-2-morpholinopropiophenone can be found in the FT-IR spectrum of the condensate residue from the peak zones. The matches can be seen at 2953 cm<sup>-1</sup>, 2853 cm<sup>-1</sup>, 1584 cm<sup>-1</sup>, 1258 cm<sup>-1</sup>, and 923.5 cm<sup>-1</sup>, among others (Figures 9 and 10).

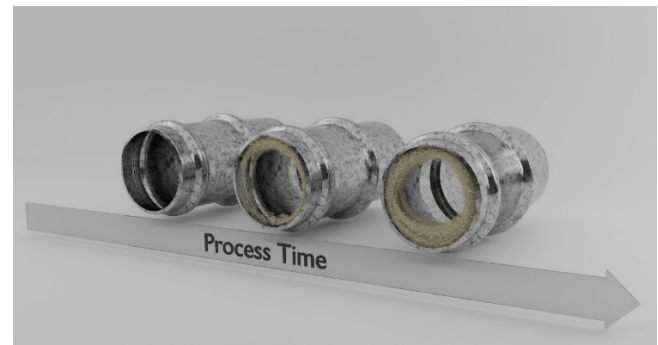


**Figure 9.** Peak Correlations of =CH<sub>2</sub> Valence Vibration Between 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (light blue curve) and Condensate Samples (green curve – inlet area, red curve – peak area, blue curve – cooling area)



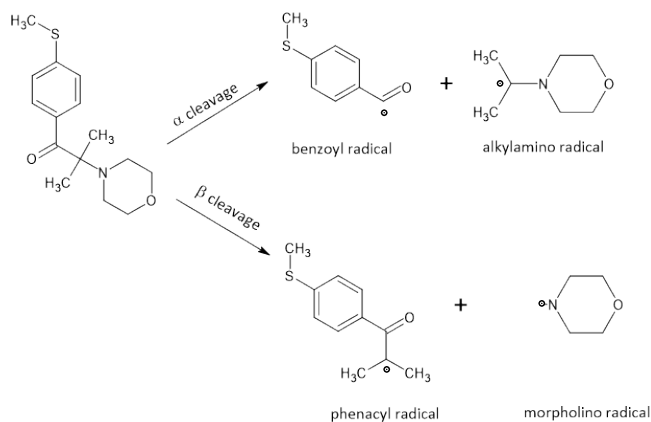
**Figure 10.** Peak Correlations Between 2-methyl-4'-(methylthio)-2-morpholinopropiophenone (light blue curve) and Condensate Samples (green curve – inlet area, red curve – peak area, blue curve – cooling area)

The 2-methyl-4'-(methylthio)-2-morpholinopropiophenone outgasses from the solder mask during the reflow soldering process and can subsequently crystallize in the flow-calming areas of the soldering machine, such as pipes or at areas of flow discontinuity at suitable temperatures over the entire process time (Figure 11).



**Figure 11.** Crystallization of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone from the Solder Mask During the Process Time in Reflow Soldering Process

If the photoinitiator can be identified in the condensate residue, this often indicates a quality problem in the finished assembly. The reason for this is the fact that the photoinitiator triggers a polymerization and crosslinking reaction of the soldermask in the manufacturing process. If this reaction is predominantly complete, then the photoinitiator is bound and cannot be detected in the condensate residue. There are two possible causes for its presence in the condensate residue. The first cause is the presence of oxygen during the coating of the soldermask. The molecule of the photoinitiator (Figure 12) breaks down into two parts under UV irradiation. Each half of the molecule can initiate a radical polymerization reaction and enable acrylate molecules (monomers) to grow into longer molecular chains (polymerization).



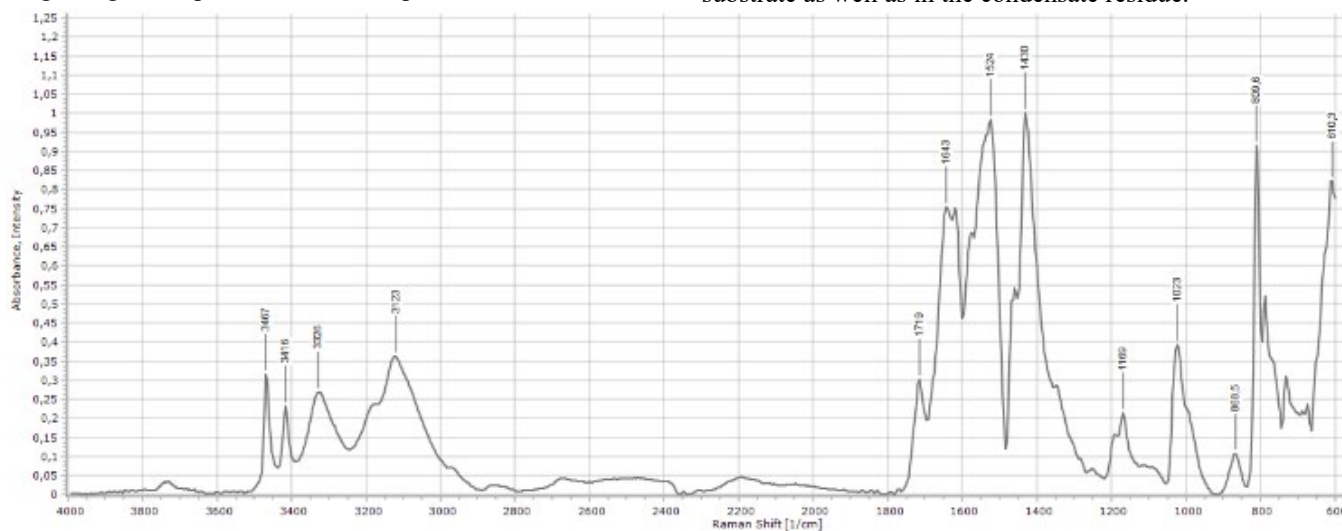
**Figure 12.**  $\alpha$  and  $\beta$  Cleavage of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone

Oxygen inhibits this reaction by binding to and blocking the reactive ends of the photoinitiator immediately after the UV-initiated decomposition of the photoinitiator. Thus, although the photoinitiator is present in the soldermask, it could not initiate a sufficient polymerization reaction. The result is an incompletely polymerized and crosslinked soldermask with an ostensible good quality. The second possible cause for outgassing of the photoinitiator is its presence in excess.

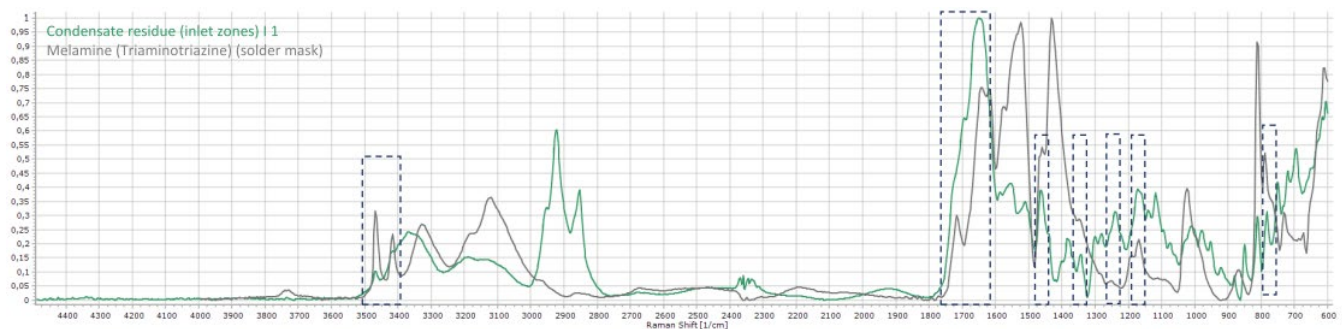
In this case, the decomposed photoinitiator is physically present in the soldermask without being able to initiate a reaction, as no suitable reaction partners are available. This case can also result in increased outgassing of the photoinitiator in the soldering process.

### Triaminotriazine

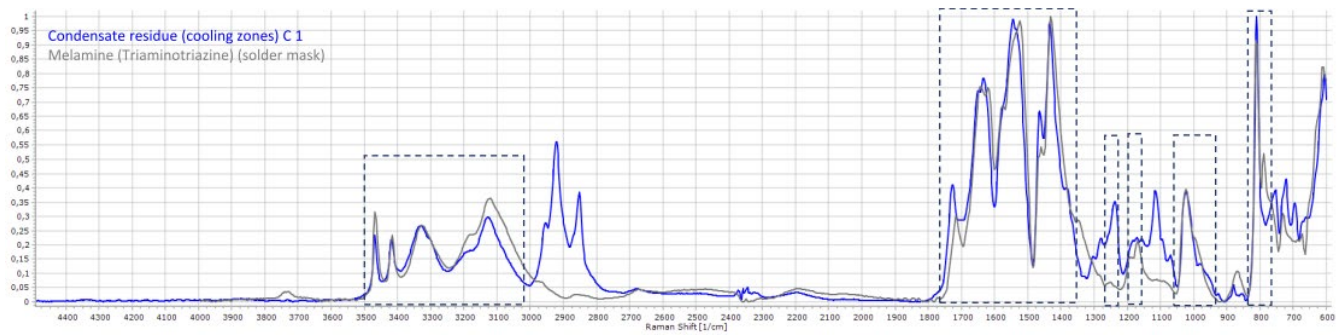
Spectrum comparison of the condensate residue from the inlet area (Figure 14) and the cooling area (Figure 15) with the triaminotriazine (Figure 13) shows clear correlations. The prominent characteristic in the range of  $3500\text{cm}^{-1}$ - $3000\text{cm}^{-1}$  is clearly visible in condensate samples from the inlet zone and the cooling zone. Most importantly, the spectrum of the condensate residue from the cooling zones also shows correspondence with the spectrum of triaminotriazine in the range of  $1780\text{cm}^{-1}$  -  $1360\text{cm}^{-1}$ . The peak at  $1650\text{cm}^{-1}$  can be assigned to the  $-\text{NH}_2$  oscillation [2]. Condensate sample from the inlet area shows a strong peak here, while the  $-\text{NH}_2$  oscillation of the sample from the cooling area is only visible as a shoulder. At  $1281\text{cm}^{-1}$ , C-N valence vibration can be observed in all samples. The peak here is significantly stronger than in the spectrum of the pure substance of triaminotriazine, indicating possible further chemical reactions that have taken place in the printed circuit board substrate as well as in the condensate residue.



**Figure 13.** FT-IR Spectra of Triaminotriazine

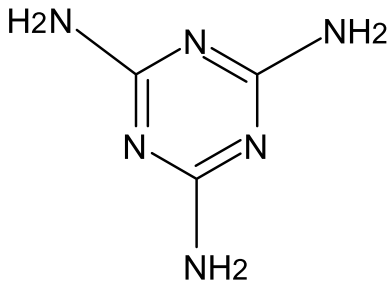


**Figure 14.** FT-IR Spectra of Condensate Residue from Inlet Area in Comparison with Triaminotriazine



**Figure 15.** FT-IR Spectra of Condensate Residue from Cooling Area in Comparison with Triaminotriazine

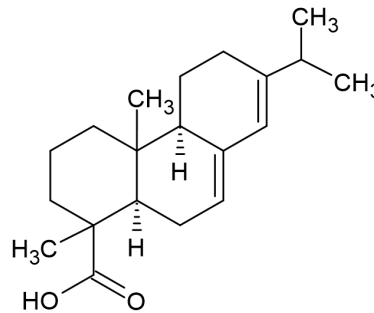
Chemical components containing triaminotriazine (Figure 16) or constituents thereof in their molecular structure are most probably outgas from the PCB substrate or from solder resist during the soldering process. Since the melting temperature of triaminotriazine is above 280°C, it can be assumed that this substance outgases in the peak zones of the soldering machine and condenses with the process gas in the inlet and cooling zones.



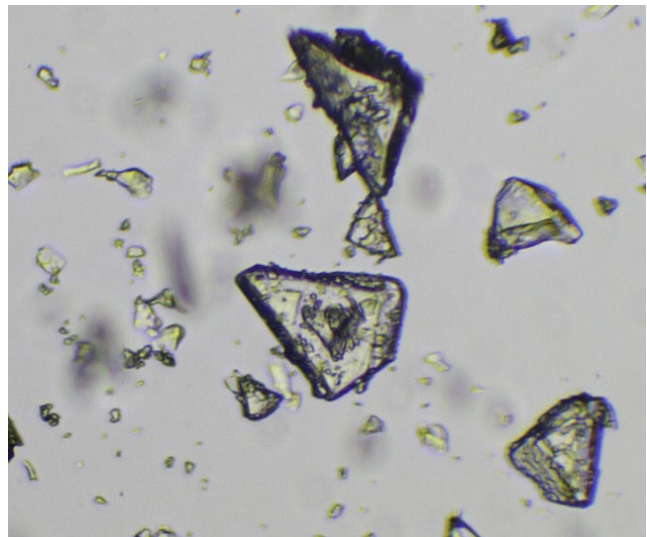
**Figure 16.** Chemical Formula of Triaminotriazine

#### Rosin and its reaction products

In all condensate samples, but especially in samples from the inlet areas, a clear signature of the rosin is visible. Depending on its composition, the rosin becomes gaseous in a temperature range from approx. 139°C to approx. 165°C. The rosin outgases into the soldering atmosphere in the inlet zones. Rosin, especially abietic acid and its derivatives, are components of various solder pastes. They outgas before the solder paste melts and support the formation of an intermetallic layer by removing the oxidation from the solder pad. Abietic acid molecule is a formation of 3 rings with 4 methyl groups and one carboxylic acid group (Figure 17). It is present in crystalline form as shown in Figure 18.



**Figure 17.** Chemical Formula of Abietic Acid



**Figure 18.** Crystals of Abietic Acid, 400x Magnification

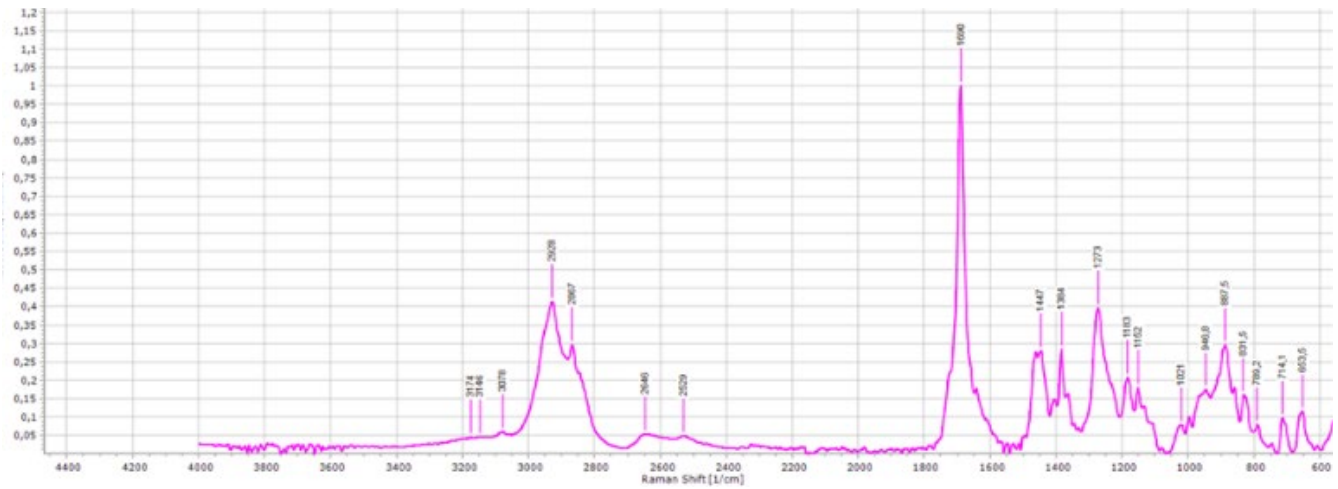


Figure 19. FT-IR Spectra of Abietic Acid

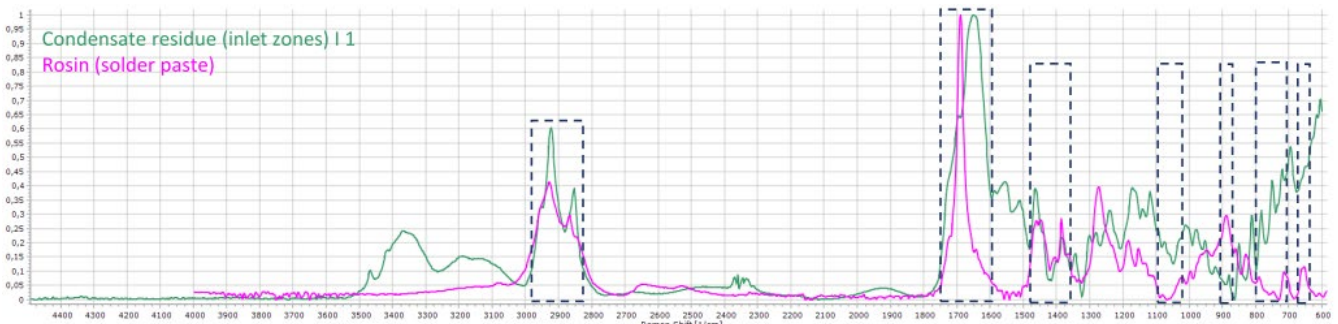


Figure 20. FT-IR Spectra of Condensate Residue from Inlet Area in Comparison with Abietic Acid

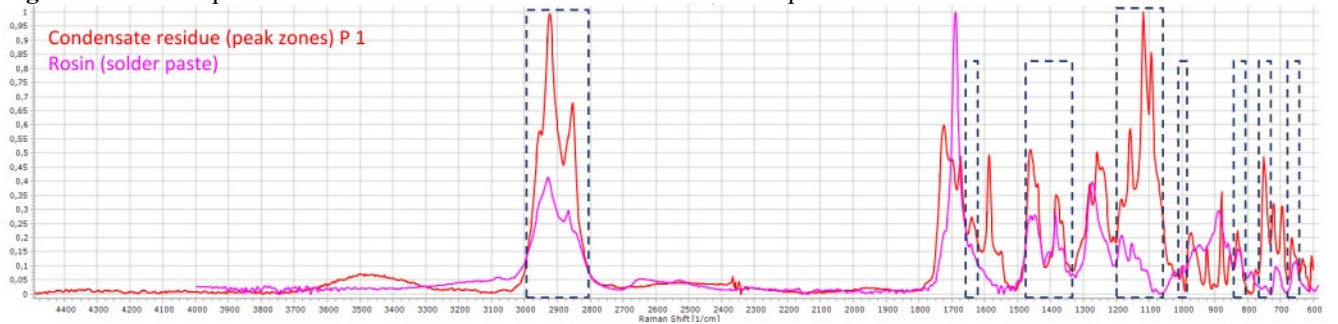


Figure 21. FT-IR Spectra of Condensate Residue from Peak Area in Comparison with Abietic Acid

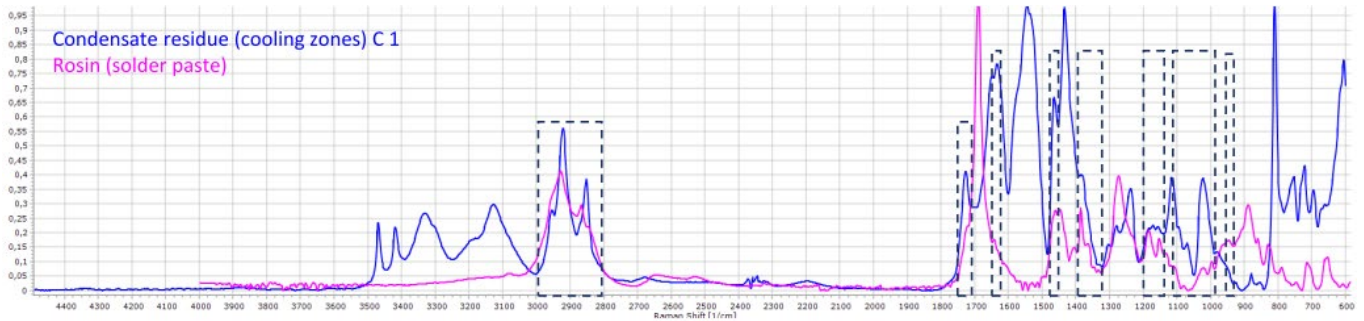


Figure 22. FT-IR Spectra of Condensate Residue from Cooling Area in Comparison with Abietic Acid

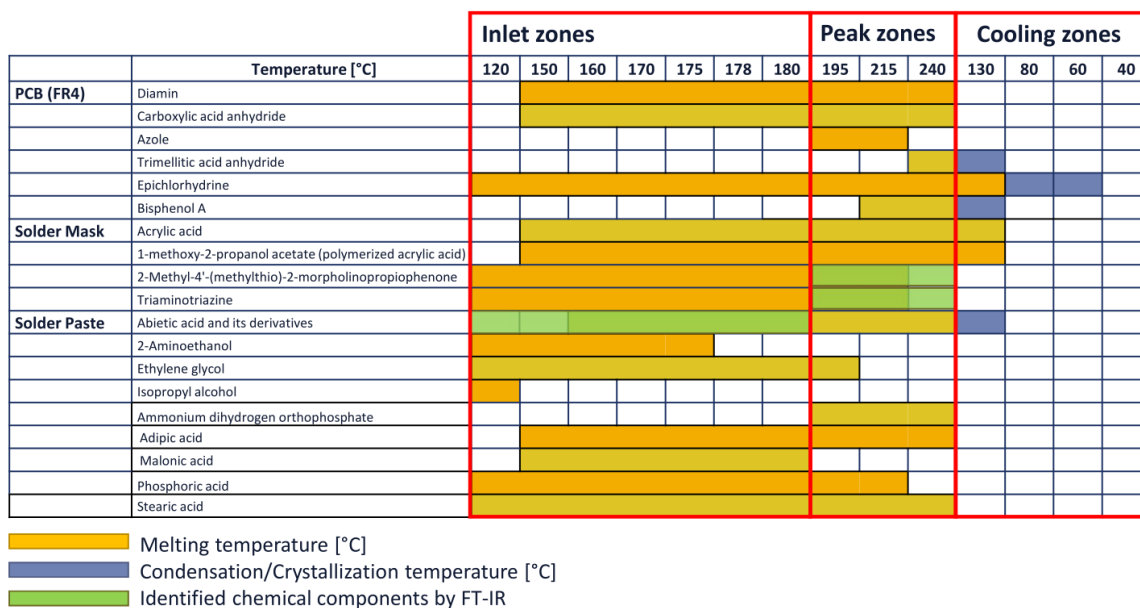
The peaks of rosin are clearly visible in the spectrum of the condensate residue. Numerous corresponding peaks are found in the spectra of rosin and condensate residues.

They are located at wave numbers  $1727\text{ cm}^{-1}$ ,  $1463\text{ cm}^{-1}$  and at  $1382\text{ cm}^{-1}$ . The peak at  $1727\text{ cm}^{-1}$  can be clearly assigned to the carbonyl acid group  $\text{-COOH}$ . The Peak at  $1463\text{ cm}^{-1}$  is a valence vibration of  $\text{-CH}_2$  group.

## SUMMARY

Condensate samples from the inlet area, the peak area and the cooling area of a reflow soldering system are clearly different in their molecular signature. This is confirmed by the theoretical study of the previous paper "Detailed Study of Condensate Residues - Analysis of the Responsible Reaction Partners as well as Reasons for Condensate Polymerization and Growth of Crystalline Structures in the Soldering Process". Figure 23 gives an overview of the possible molecular components from the solder paste, printed circuit board and solder resist, which can outgas in the soldering process and react, polymerize and crosslink with each other depending on the reaction partner and temperature range. Three main substances could be identified by the FT-IR analyses of the condensate residue. The condensate residues showed significant correlation in their molecular signal with the pure substances "2-methyl-4'-(methylthio)-2-morpholino

propiophenones", "triaminotriazine" and "rosin". Based on the melting temperature of the identified substances, it can be assumed that the temperature range of the outgassing is not necessarily correlated with the soldering zone in which the condensate residue has the highest concentration of the substance. On the one hand, the reason for this is the distribution of the soldering atmosphere in the soldering machine (extraction from the various zones and a redistribution of the soldering atmosphere, condensate management, etc.), but on the other hand it also depends on the size and reaction speed of the outgassing molecules that interact with each other. This is also demonstrated by the fact that, for example, crystalline growth of 2-methyl-4'-(methylthio)-2-morpholinopropiophenone takes place in a different area of the soldering system than the outgassing of its starting components.



**Figure 23.** Overview of the Possible Molecular Components from the Solder Paste, Printed Circuit Board and Solder Mask

## REFERENCES

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- [2] Manfred Hesse, Herbert Meier, Bernd Zeeh, „Spectroscopic methods in organic chemistry“, Georg Thieme Verlag KG, Stuttgart, 2005, pp. 40-58.