

Pre-Ignition Fire Detection Using Semiconducting Metal Oxide Gas Sensors – Experimental and Chemometric Investigations

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Abstract

The issue of insufficient technology for smoke or fire detection in habitable spacecraft was the main motivator for this work. Due to complex shapes, sizes, and movements of particles and agglomerates in microgravity and forced convection, the requirements for detectors differ from terrestrial application. As a consequence, frequent false alarms decrease the alertness of the crew on missions. Regular deactivation of the detection system, as currently practiced during cleaning activities on the International Space Station (ISS), is an unsatisfactory solution. The current detector's lack of sensitivity toward small particles generated from overheated spacecraft materials, as revealed by experiments, makes innovation all the more necessary. This work documents the first steps in the overall project to develop a suited pre-ignition fire detection system.

With the key limitation of time, **pre-ignition** fire detection is targeted using highly sensitive, small, power-efficient, and fast semiconducting metal oxide (SMOX)-based sensors. As the main component of the detection system, the commercially available sensor SGP40 (Sensirion AG, Switzerland) was chosen and investigated, to address the current issues on the ISS and more crucially, the arising obstacles, caused by planetary dust in future missions to the Moon and Mars. Poly(methyl methacrylate) (PMMA), poly(dimethylsiloxane) (PDMS), Nomex[®] IIIA, and Kapton[®] were selected as materials used in space applications and their thermal behavior and outgassing analyzed. A test-apparatus was built to facilitate the detection experiment, while doubling as a multi-purpose and future relevant gas mixing system. The design and development process as well as information on the construction and software are documented as part of this work to support maintenance and promote adaptations to the needs of scientific tasks. The polymers were heated in a controlled manner, in a specialized tube furnace, and the thermally-driven outgassing measured the SGP40 sensors, in constant and temperature modulated operation. In combination with suited chemometric methods, predictions on material temperatures resulted in mean absolute errors of 4.74 % for PMMA, 5.52 % for Nomex[®] IIIA, 14.20 % for PDMS, and 14.94 % for Kapton[®]. Mean

relative errors ranged from 3 K to 10 K, using random forest regression. Additionally, the materials' relevant characteristics of degradation temperature and outgassing species were assessed using thermogravimetric analysis-mass spectrometry (TGA-MS) and gas chromatography-mass spectrometry (GC-MS). Further investigations on the ability of the commercial sensor were conducted, to deliver spatial information on a source. For this purpose, 32 sensors were distributed in a chemical sensor grid, in the 1 m³ test volume of the test-apparatus, in an attempt to localize the origin of heated PMMA in a three-class classification. The patterns of the sensor responses led to a classification accuracy of 100 % using dynamic time warping distances with the k-nearest neighbors algorithm. Furthermore, information on the plume movement was gained, leading to the identification of optimal sensor placement in the present configuration.

The results of this work form the basis for further development of pre-ignition fire detection, while the specialized test system will remain in use beyond the scope of the project.

Zusammenfassung

Aufgrund der unzureichenden Möglichkeiten, die derzeit zur Branddetektion in bemannten Habitaten im All zur Verfügung stehen, beschäftigt sich diese Arbeit mit der Entwicklung einer Alternative zu der gebräuchlichen Partikeldetektion. Durch fehlende Sedimentation in Mikrogravitation, sowie die Agglomeration der Partikel in der erzwungenen Konvektion an Bord, kommt es zu veränderten Anforderungen an die Detektoren, im Vergleich zu terrestrischen Anwendungen. Beispielsweise konnte in einer Experimentreihe die unzureichende Detektion, des auf der Internationalen Raumstation verwendeten optischen Detektors, gegenüber kleiner Partikel, emittiert von erhitzten Raumfahrtwerkstoffen, festgestellt werden. Angesichts des enormen Risikos, das in dem abgeschlossenen Volumen eines Weltraumhabitats von den bei einem Brand entstehenden Gase ausgeht, ist eine schnelle Reaktion, möglicherweise sogar Evakuierung, entscheidend für das Überleben der Besatzung. Zudem führt wiederholte Detektion von Staub und anderen Partikeln zu Fehlalarmen, welche die Alarmbereitschaft der Crew erheblich beeinflussen und kurzzeitige Deaktivierung der Lüftung sowie sorgfältige Protokollierung der Situation nach sich ziehen. Die Problematik könnte sich möglicherweise nach dem Ende der Internationalen Raumstation weiter zuspitzen, da durch die geplanten Missionen zum Mond und Mars planetare Stäube in die Habitate gebracht werden könnten. Die derzeitige Maßnahme, um während der regelmäßigen Reinigungen keine Fehlalarme zu provozieren, ist die simple Abschaltung der Detektoren.

Diese Arbeit beschreibt die ersten Schritte in der Entwicklung eines Systems zur Detektion während der Entstehungsphase eines Brandes, **vor** Entzündung und dem Entstehen einer Flamme. Definiert durch die Zeit als entscheidende Ressource, sowie die Anforderungen an Energieverbrauch, Masse und Volumen, überzeugen miniaturisierte Metalloxid-Halbleitersensoren (SMOX) als Hauptkomponenten des zu entwickelnden Systems. Durch ihre hohe Sensitivität gegenüber flüchtigen organischen Stoffen, welche abhängig von der Temperatur aus Polymeren entweichen, sind die kommerziellen Sensoren SGP40 (Sensirion AG, Schweiz) geeignete Kandidaten.

Als Testmaterialien wurden die in der Raumfahrt verwendeten Kunststoffe Polymethylmethacrylat (PMMA), Polydimethylsiloxan (PDMS), Nomex[®] IIIA und Kapton[®] gewählt. Erkenntnisse, über aus den Materialien ausgasende Spezies sowie Zersetzungstemperaturen, wurden mittels Gaschromatographie-Massenspektrometrie und thermogravimetrischer Analyse gewonnen. Ein Großteil der Arbeit beschreibt die Entwicklung einer geeigneten Testanlage zur Durchführung der Detektionsexperimente. Um die Anlage auch in zukünftigen Arbeiten möglichst vielseitig verwenden zu können, wurden einige Funktionalitäten (wie beispielsweise automatisierte Lüftung und die Injektion von Analyten) eingerichtet und deren Entwicklung sowie nachfolgende Validierung dokumentiert. In diesem Aufbau, unter Verwendung eines Rohrofens, wurden die Testmaterialien und die Sensorantworten der SGP40 ausgewertet. Durch Modellierung der Betriebstemperatur der Sensoren, unter Verwendung chemometrischer Methoden, konnten gewonnene Modellvorhersagen präzisiert werden. So gelang es mittlere relative Fehler zwischen realen Temperaturen und Vorhersage von 4.74 % für PMMA, 5.52 % für Nomex[®] IIIA, 14.20 % für PDMS und 14.94 % für Kapton[®] zu erreichen. Die mittleren absoluten Fehler der Random-Forest-Regression liegen zwischen etwa 3 K und 10 K. Zur Evaluierung des Potenzials des SGP40 eine Gasquelle zu lokalisieren, wurde in der genannten Testanlage eine Machbarkeitsstudie mit PMMA als repräsentativen Werkstoff durchgeführt. Dabei wurde der Rohrofen zwischen drei möglichen Positionen verschoben, und die entstehenden Gase wurden mit 32 im 1 m³ großen Testvolumen verteilten Sensoren gemessen. Nicht nur konnten mittels dynamischer Zeitnormierung und k-Nächste-Nachbarn-Algorithmus unter Leave-One-Out-Kreuzvalidierung 100 % der Positionen richtig zugeordnet werden, das Experiment lieferte auch wichtige Einblicke in die Bewegungen der Gaswolke und die hierdurch mehr oder weniger geeigneten Sensorpositionen.

Durch die in dieser Arbeit gesammelten Informationen wurde die Basis für die Entwicklung eines Systems zur Detektion während der Entstehungsphase eines Brandes geschaffen und entsprechend weitere Schritte konkretisiert. Neben den gewonnenen Erkenntnissen, wurden Hard- und Software für die Testanlage entwickelt und dokumentiert, welche weiterhin für das Projekt der Branddetektion sowie darüber hinaus Anwendung in verschiedenen Bereichen der Gassensorik finden werden.

1 Introduction and Motivation

Since the 1961 launch of the Vostok 1, sending the first human to space [1], the technology for habitable spacecraft has continuously improved. Environmental Control and Life Support Systems (ECLSS), which are responsible for sustaining a healthy breathable atmosphere, temperature and humidity control, water and food supply, ventilation, fire safety, and waste management, have evolved in the last decades from supporting the first very short space missions to enabling permanently occupied stations like the ISS [2]. Nevertheless, many challenges remain, particularly for missions into deep space, beyond Low Earth Orbit (LEO). Identified as one of these challenges, substantial for future missions in human spaceflight, is advancing research on fire safety [3, 4]. While Meyer and Ulrich [5] describe a spacecraft fire as “one of the most catastrophic emergencies“, a 2022 review study by Guibaud et al. [6] reports 12 past fire or smoke incidents related to manned space exploration. None out of the five electrical failures on the Space Shuttle Orbiter (1981–2011) resulted in actuation of the deployed ionization smoke detectors [7–9]. Furthermore, six false alarms and five built-in test failures were documented [10]. Stable laser-diodes were available during the time of the development of the ISS, allowing for more power efficient detectors based on light-scattering, sensitive towards particles larger than $0.3\text{ }\mu\text{m}$ [9, 11]. According to Guibaud et al. [6], none of the five crewed space programs active in 2021 reported any significant fire-related issues. Yet, the evaluation of the Smoke Aerosol Measurement Experiment (SAME) (conducted in an uncrewed spacecraft after departure from the ISS), comparing the two aforementioned smoke detectors, demonstrated the lack of sensitivity of the ISS detector to a substantial number of Kapton[®] and Teflon[®] smoke samples. The Space Shuttle detector revealed issues detecting Kapton[®], Teflon[®], and lamp wick. Out of all materials tested, Teflon[®] and Kapton[®] exhibited the smallest smoke particles [12].

Both types of detectors aim to detect smoke. Ionization detectors ionize the air (O_2 and N_2) by emitting alpha particles. Between two detector plates, a constant ion current is

established, dependent on size, mass and number of ionized molecules. When dust or smoke particles enter the current, they attach to the ions and the current decreases.

Photoelectric detectors (installed across habitable modules on the ISS) emit a laser beam of near infrared, reflected by mirrors onto a photodiode. A second photodiode in a 30° angle detects light, scattered by particles in the path and creates a signal, which after exceeding a threshold, invokes an alarm [6, 11, 13].

Several particles, found airborne in the ISS, ranging from 150 nm in diameter to larger sized objects are prone to continuously enter the detection volume due to the absence of sedimentation. While it is well known that such incidents occur, they are usually not reported in publicly available records [13]. Titanium dioxide, fume-like metal particles, metal wear particles, antiperspirant particles, human skin flakes and clothing lint were identified among others [14, 15]. When such particles trigger an alarm, the procedure for the ISS is a full fire response, until verified as false. This includes adjusting ventilation and documenting the incident, in addition to the necessary steps to return to normal operation. Consequently, false alarms result in interruptions and additional work. Besides, repeated false alarms lead to the decreased alertness of the crew as a natural and human reaction. On future missions, lunar and planetary dust is expected to add to this problem. Planned missions by the National Aeronautics and Space Administration (NASA) to the Moon and Mars, pose the question of fire safety in regard to the expected increase in false alarms with Moon and planetary dust accumulating after extravehicular activity [13]. In conclusion, the technology presently employed meets terrestrial requirements, but lacks sufficient accuracy in microgravity environments.

Crucial in every event of fire, even more so in enclosed habits, is time. The earlier the detection, the higher the chances to extinguish the fire or evacuate. As soon as the toxic products from combustion are formed, the fire poses a serious health risk. Modified polymers, which are vastly deployed, are currently difficult to differentiate from dust or to detect at all if the combustion particles or agglomerated are of small size. The detectors investigated in the last experiment of the Spacecraft Fire Safety Demonstration Project (Saffire VI) showed response to burning PMMA only after most of the toxic products were released [16]. Consequently, measuring the materials' early outgassing, at slightly elevated temperature before ignition and release of decomposition products, could pave the way for safe detection of heated materials in different habitats. SMOX-based gas sensors could be a suitable candidate, because of their outstanding

sensitivity and excellent response time, necessary for safety applications [17, 18]. Heiland was the first to report gas sensitive properties of a semiconducting metal oxide in 1954 [19]. Later, Taguchi patented the first commercially available sensors, which were sold by the Japanese company Figaro [20]. Up to the present time, SMOX-based gas sensors continue to be investigated, focusing on aspects such as fundamentals of the involved chemistry and physics, the possibilities to improve the sensing properties by different synthesis routes, annealing procedures, or the incorporation of additional foreign atoms using doping or loading. One of the greatest drawbacks and researched property is the lack of selectivity, excluding many unmodified materials from application fields, where only one known target gas is aimed to be measured [18, 21, 22]. Concomitantly, the lack of selectivity and therefore interaction with a large range of gases can be an incredible advantage. SMOX-based sensors are used in many areas, including complex environments like indoor and outdoor air, food industry, medicine and numerous additional fields [23–25]. In many of these applications, the miniaturized low-cost sensors are combined in complementary arrays, tailored for the use-case. In addition to increasing the number of sensors, the existing sensors can be operated in a cyclic fashion at varying temperatures. By modulating the operating temperature of the material, complex changes in kinetics and intermediate non-equilibrium states are provoked [26], leading to a great gain in information, improved selectivity [27], and reduction of power consumption [28]. This technique has proven to be revolutionary for many applications and is still investigated in regard to the actual mechanisms and importance of the temperature sequence [27, 29].

SMOX sensors with their high sensitivity, low cost, and small size, show valuable advantages for the deployment in a chemical sensor grid (CSG) used for gas source localization (GSL) in spatially constraint environments [30]. While the use of semiconducting metal oxide gas sensors in early outgassing of modified polymers has been researched to some extent and investigated for their ability of gas source localization, the combination of both is rare.

For instance, Han et al. [31] identified dioctyl phthalate and 2-ethylhexanol as reliable signature gases, released from nine different heated polyvinyl chloride (PVC) cables, detectable by a metal oxide gas sensor from SnO_2 . Early detection of outgassing from heated PVC was also achieved with WO_3 and In_2O_3 [32]. Wang et al. [33] used a variety of materials, including four boards and two types of cables, to verify the feasibility of gas detection in their detection system with an olfactory unit consisting of six

SMOX sensors. Further, they compared multiple machine learning algorithms in their performance at different stages of heating. Ming et al. [34] used a sensor array of two SMOX sensors and one electrochemical sensor to distinguish PVC, Teflon®, Kapton®, and silicone rubber, used as electrical wires.

Using a three-dimensional sensor grid of 27 calibrated SMOX sensors, Burgués et al. [35] visualized the temporal gas distribution of evaporated ethanol and detected bout frequency as a useful measure for source localization. They based their calculations on this measure on earlier findings by Schmuker et al. [36], who decoded information delivered by metal oxide gas sensors to identify the distance from turbulence-induced fluctuations of different gases in a wind-tunnel at different speeds.

1.1 Scope of Work

This work investigates temperature-dependent outgassing from selected polymers used in space applications, with the aim to determine whether the commercial SMOX-based gas sensor SGP40 is capable of detecting the emitted species. Beyond overheating detection, the study focuses on the prediction of material temperature, based on temperature-dependent gas signatures. A key challenge addressed, is the localization of the complex gas mixture of one heated material, serving as a representative case study.

Chapter 2 *Fundamentals and Literature* provides a background and introduces the fundamental concept of the here aimed detection of temperature-driven outgassing from polymers. Additionally, it delivers the basics of the analytical methods utilized in this work and presents different machine learning models applied to both temperature-modulated sensors and sensors operated at constant temperatures.

As one of the key elements in analytical chemistry is sampling, a large part of this work was devoted to the construction and characterization of the Ambient-air Sensor Training and Research Apparatus (ASTRA). This system was designed as a modular, multi-purpose platform to fulfill the requirements of the presented research and support potential future applications in the domain of environmental studies and gas sensors. The hardware, functionality and software are reported in Chapter 3 *Material and Methods*, in addition to Chapter 4 reporting about the systems performance and the evolution of analyte concentration over time, during different operational modes.

Chapter 5 *Temperature Predictions* presents the results obtained by the temperature-controlled measurements on PMMA, PDMS, Nomex[®] IIIA and Kapton[®], while Chapter 6 *Sample Analysis Using GC-MS* provides an analysis of the materials' outgassing. *Sensor Network-Based Gas Source Localization and Distribution Analysis* outlines measurements performed with 32 spatially distributed sensors within the ASTRA, to investigate the feasibility of gas source localization and gas plume mapping. All chapters reporting the results conclude the relevant findings, while Chapter 8 *Summary and Outlook* establishes a link and delivers a perspective on the measurement apparatus, the obtained results, and the future objectives in the development of the sensor system.

2 Fundamentals and Literature

This section provides the theoretical background on the operating principle of the sensors used, the models utilized as well as the theories this research is based on.

2.1 Scientific Basis of Temperature-Induced Outgassing

Synthetic polymers on their own are usually not suited for industrial use as plastics*. To improve their properties and tune them for application, different additives are used. The two main objectives are to improve thermal stability and allow melt processing, and to improve the properties like long term durability, color, flexibility, and impact resistance. The third main objective is the correction of the unwanted properties, resulting from the additives added for the first two objectives [37].

The most used additives can be categorized in plasticizers, flame retardants, stabilizers (antioxidants and UV stabilizers), heat stabilizers, slip agents, lubricants, curing agents, blowing agents, biocides, colorants, pigment fillers and reinforcements [38]. Generally, additives can be incorporated in the polymer matrix during different processing steps. Often, so called masterbatches, containing a mixture of concentrated additives are used. For special applications, a reaction between the additive and the polymer is contributing to the properties of the plastic, but in most cases the additives are not chemically bound to the polymer chain [38, 39]. This distinction is explained using the example of plasticizers, as they are the most common additives.

The first use of a plasticizer was reported to be 24000 BC when humans formed clay figures using water to improve the materials pliability. Now they are used mainly to decrease the glass transition temperature, to make the polymer flexible and processable. Other advantages of adding plasticizers are control over viscosity, chemical reactivity, flammability, smoke production as well as gas permeability [40]. The additives can

* Plastics are generally named by the base polymer (if they do not have a brand name), even if additives are present as secondary ingredients.

be classified in two groups: internal plasticizers and external plasticizers. **Internal plasticizers** are incorporated in the polymer structure. An internal plasticizer can be introduced as a monomer by copolymerization, creating a less ordered polymer structure and changing the thermal properties of the resulting copolymer. The added monomers are chemically bound in side groups or the main chain of the polymer.

In commercial application, **external plasticizers** are most frequently used, allowing for more flexibility in the manufacturing. They do not chemically react with the polymer but are situated in between chains of the polymer matrix [41, 42]. In Figure 2.1, the theories to explain plasticizers in polymers are visualized. The lubricity theory states that the plasticizer molecules act as lubricant for the polymer chains to move freely when force is applied. The theory assumes surface irregularities of the polymer impeding this movement without the plasticizer. The gel theory holds that a gel structure is formed by plasticizers interacting with the polymer structure. The plasticizers can solvate and de-solvate at different sites. This explains the increased softness with increasing temperature, which is not found to this extend for internally plasticized plastics. The free volume theory assumes that the free volume generated from the motion of the polymer (end groups, side groups, back bone) is increased by adding plasticizer molecules. The molecules themselves can move and create free volume, increasing the polymer’s glass temperature and plasticity [43].

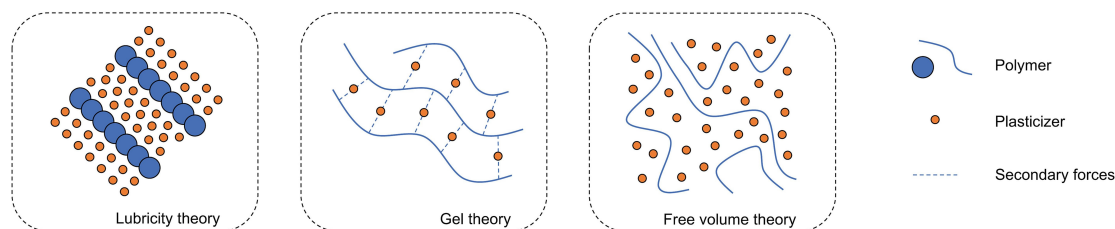


Figure 2.1: Plasticization visually explained by three theories. Adapted from [44]*.

A key limitation of external plasticizers is that unbound plasticizer molecules can migrate or evaporate from the polymer matrix over time, leading to increased brittleness and reduced flexibility. In addition, such migration may pose potential health risks, particularly when plastics come into contact with food or biological fluids [46].

* Adapted from A. Bonifacio, L. Bonetti, E. Piantanida, L. De Nardo, Plasticizer design strategies enabling advanced applications of cellulose acetate, *European Polymer Journal*, 2023, 197: 112360, © 2023 The Author(s), licensed under CC-BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>); based on [45].

The extent of additive loss from polymers is influenced by solubility, concentration, and volatility. Thus, larger, more flexible additives are generally preferred, however, thermal aging at elevated temperatures can significantly accelerate additive depletion [47, 48]. Using thermogravimetric analysis coupled with Fourier transform infrared spectroscopy, Cuthbertson et al. [49] demonstrated that additives can be clearly identified even at low percentage weight loss, confirming the relevance of additive release.

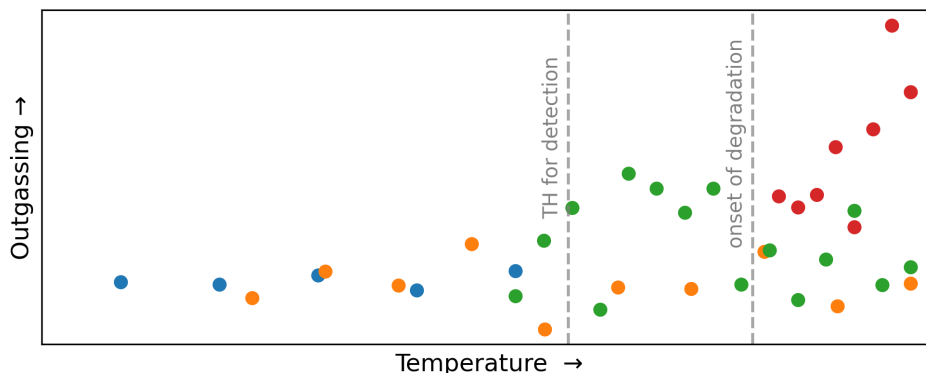


Figure 2.2: Conceptual illustration* of temperature-dependent outgassing: increasing temperature leads to higher concentration and broader range of released species.

Building on these mechanisms, the concept for detecting heated plastics in this work is based on measuring the chemical interaction between a SMOX-based gas sensor and the surrounding atmosphere containing polymer exhaust. As described above, polymer emissions are thermally driven, and the type and quantity of released substances depend strongly on material temperature. At low temperatures, unbound residual monomers, solvents, or processing additives are released primarily through surface desorption or diffusion through the polymer matrix. At moderate temperatures, molecules located between polymer chains are increasingly released due to enhanced molecular mobility, and at higher temperatures thermal degradation products begin to form [50]. The temperature threshold at which these processes occur depends on both the additive properties and the polymer matrix. Following this logic, and as illustrated in Figure 2.2, increasing the temperature is expected to result in both a higher emission rate and a broader spectrum of released chemical species, which can subsequently be detected by gas sensors.

* Illustrations were created using `draw.io`, `Inkscape`, `PowerPoint`, and `Python`.

An ideal pre-ignition detection system should therefore be capable of identifying the hazard of overheated materials and, where possible, localize the source of outgassing at moderate temperatures. Modified polymers were selected as the primary emission source in this study due to their ubiquity in modern environments.

2.2 Gas Sensors

Gas sensors are characterized by their ability to qualitatively and/or quantitatively characterize surrounding gases. To compare different sensor types, metrics like *sensitivity* and *selectivity* are commonly consulted. The sensitivity of a device is the magnitude of change in sensor signal upon the change in concentration of the target gas, which can be calculated as the slope of the calibration curve [51]. Due to the allometric relation between concentration and resistance of SMOX gas sensors, as discussed in detail in [52], the sensitivity is concentration dependent. The selectivity of a sensor describes its ability to measure a specific analyte, independent of the presence of other analytes and is often used as a qualitative metric. In other words, it describes the lack of interfering reactions or lack of cross-sensitivity [51]. In contrast to SMOX based gas sensors, electrochemical sensors with liquid or polymer electrolyte are often not as robust, yet they typically show higher selectivity. Additionally, the sensor signal of amperometric gas sensors is proportional to the concentration of the measured analyte [53].

Semiconducting Metal Oxide Gas Sensors

SMOX-based gas sensors are chemoresistive sensors. The sensitive metal oxide-based layer is acting as the receptor. A gas can either bind to the surface of the layer by chemisorption, involving the formation of a chemical bond, or physisorption, a weaker interaction driven by van der Waals forces, usually taking place at lower temperatures [54]. The process of physisorption is usually fast and reversible, while the process of chemisorption (or ionosorption in the case of direct electron transfer) often requires an activation energy, which can be delivered in form of increased temperature or light irradiation [55]. The resulting binding energy of the adsorbate is usually larger than the activation energy and dependent on the specific site, therefore, chemisorption is highly directional [54]. Often followed by this process, dissociation of the molecules or surface reactions can take place, complicating the reception mechanism [55]. The localization of electrons, resulting in a change in the number of free charge carriers, can then be read

out by suited electronics. To decrease the time to reach an equilibrium between the gas and the material surface, the sensitive layer is usually heated with a built-in heater or delivered in form of light [56].

Performance enhancement of SMOX-based sensors can be achieved in many ways. Aside from the obvious choice of different base materials, for instance SnO_2 , WO_3 , and In_2O_3 as the most used materials [51], the temperature of operation can be optimized to increase the sensitivity [57]. Additionally, the choice of synthesis route and curing can influence the materials grain size or surface properties and therefore its reactions [58, 59]. The number of defects in the material has a strong effect on sensing properties like selectivity and sensitivity as well as long term stability and can be artificially increased by doping or loading the material [21, 60].

Semiconductors can be categorized into *p*-type and *n*-type, by the dominant charge carriers. The sensor SGP40 [61], used in this work has an undisclosed composition, but is assumed to consist of *n*-type semiconductors, similar to its predecessor, reported as palladium doped SnO_2 [62]. The most widely used semiconductor type on the market is *n*-type, primarily because of the higher sensitivity, governed by advantageous transduction in oxygen-rich conditions [63]. Oxygen, present in virtually all atmospheres to which SMOX sensors are exposed to, interacts with the *n*-type metal oxide surface and forms acceptor-like surface states (similar to the behavior of other oxidizing gases) [64]. Some of the electrons from the bulk migrate towards the surface, where they are trapped in the acceptor states, forming a depletion layer close to the grain's surface [65]. As a consequence, the resistance increases due to the potential barriers, often referred to as double Schottky barriers, formed by the depleted grains. The electrons, as dominant charge carriers, have to overcome the barrier to move from one grain to the next [52]. The thickness of the depletion layer which is formed as a consequence of adsorbed electronegative species trapping electrons at the surface, is dependent on the concentration of the above-mentioned species. The charge carrier concentration in the bulk and the position of the Fermi level are not affected, if the grain size is large relative to the Debye length. Consequently, the resistance is controlled by the Schottky barriers at the grain boundaries [57, 65].

When a reducing gas, for instance carbon monoxide (as visualized in Figure 2.3), reacts with the adsorbed oxygen on the surface of the grains the gas is oxidized (in this special case forming carbon dioxide) and the electrons are released back to the grains. Therefore, this leads to a reduction of the depletion layer, lowered energy barriers and decreased resistance.

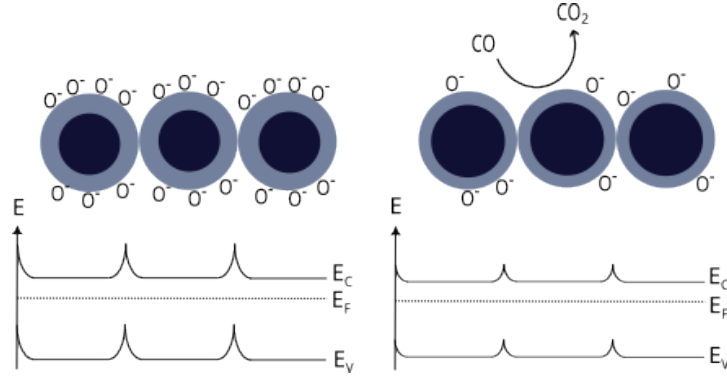


Figure 2.3: Reception of CO visualized schematically for a depletion layer controlled *n*-type SMOX.

In the case of *p*-type semiconductors, the dominant charge carriers are electron holes and the reaction with oxidizing or reducing gases leads to the converse effect in resistance compared to the above-described *n*-type.

Effect of Temperature

The amount of reactions taking place on a sensor level, is dependent on the surface available to the gas. Therefore, porous layers allow for reactions on the surface of the single grains as well as at grain-electrode, grain-substrate and grain-grain boundaries [65]. On the grain level, the reactions are dependent on the available energy. Bârsan and Weimar [65] state, that on the surface of SnO_2 at operating temperatures below $150\text{ }^{\circ}\text{C}$, the molecular-ionic (O_2^-) form of oxygen is found, whereas above that temperature species of atomic-ionic oxygen (O^- , O^{2-}) dominate. They report similar dependency of reactions on operating temperature in water vapor. Physisorbed water is only present at the surface when the temperature is below $200\text{ }^{\circ}\text{C}$. When exceeding $200\text{ }^{\circ}\text{C}$, chemisorbed hydroxyl groups can be formed increasing the surface conductivity. Further and more elaborate explanations as well as the corresponding reaction mechanisms can be found in their article [65] and references therein.

Assuming equilibrium is reached for the reactions of oxygen at the surface, an optimal

material-dependent operating temperature can be found, where a sensor delivers the highest sensitivity to a certain gas [57]. At low temperature, assuming the Schottky approximation to be valid and the charge trapped at the surface being equal to the change in the depletion layer, the density of surface acceptor states for an n -type semiconductor in air is low. At high temperature, more electrons are captured because more oxygen is ionosorbed. This is where the resistance is highest and therefore a reaction with a reducing gas like CO results in the largest release of electrons from trapped surface states. When the temperature is even higher, the n -type sensor in air will show a decrease in resistance due to thermal desorption and therefore electrons being released back to the grains.

Sensor Combination and Operation Modes

One option to increase the information accessible in a given gas composition, is by forming arrays of sensors with complementary features or reactions. Another possibility is to dynamically change the operating temperature. As touched upon on the examples of the readily present oxygen and water vapor, the temperature of the sensitive layer not only determines the reaction rate, but also facilitates different surface reactions. As a result, a sensor when operated at a low, compared to a high temperature will show different responses to selected gases due to changed reactions and kinetics thereof.

Ding et al. [66] neglect physisorbed oxygen, assuming that only chemisorbed oxygen participates in the surface reactions, while ionosorption governs the electron trapping dynamics and thus the transient conductance response of SnO_2 . By modeling the sensor response to argon and air during a modulation of operating temperature, they conclude, that the electrons move fast between valence and conduction bands, while the exchange of electrons between the conduction bands and the surface states (in the presence of oxygen) is slow and therefore contributes to the transient response found in air.

Schultealbert et al. [26] state that, due to the long time required for SnO_2 -based sensors to reach equilibrium after a temperature changes, non-equilibrium states can be deliberately utilized. Figure 2.4 visualizes this process: an immediate rise in temperature from low to high ($1 \rightarrow 2$) results in an increase in conduction (see Figure 2.4 c)), which then decreases when enough time has passed for the oxygen to ionosorb and trap electrons from the surface ($2 \rightarrow 3$). Cooling from high to low temperature ($3 \rightarrow 4$) is a fast process leading to a decrease in conductance, which increases again after relaxation of the oxygen occupation on the surface ($4 \rightarrow 1$), due to the release of trapped electrons back into the grains. This process can be seen in Figure 2.4 a) as a decrease in the depletion layer of the grains. The Arrhenius plot in Figure 2.4 b) visualizes the conductance of the transient states as solid lines and the conductance of the steady states as dashed lines. The increase in conductance during the fast rise from $1 \rightarrow 2$ results in an increase in conductance (vice-versa for $3 \rightarrow 4$) before the relaxation of the oxygen occupation and therefore constant depletion layer thickness and Schottky barrier. From $2 \rightarrow 3$ the size of the depletion layer changes (as well as for $4 \rightarrow 1$) caused by change in acceptor state density on the surface. Therefore, the energy barrier is changing as well.

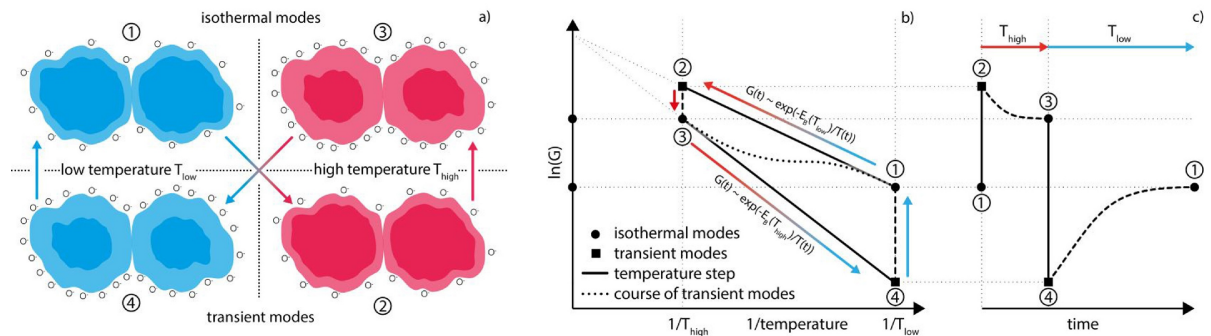


Figure 2.4: Schematic of the changes between transient and isothermal modes during the change of operating temperature between high and low: a) on grain level, b) in an Arrhenius plot of the conductance, c) conductance as a function of time. Reprinted from [26]*.

The full range of processes taking place is therefore very complex and dependent on the history of the sensor, even more so in atmospheres consisting of gas mixtures. In summary, temperature modulation allows for the use of these otherwise inaccessible

* Reprinted from Sensors and Actuators B: Chemical, Vol. 239, C. Schultealbert, T. Baur, A. Schütze, S. Böttcher, T. Sauerwald, A novel approach towards calibrated measurement of trace gases using metal oxide semiconductor sensors, 390-396, Copyright (2017), with permission from Elsevier; based on [67, 68].

transient modes, which are characteristic for each sensor type and analyte gas [69]. Temperature modulations have shown to be successful in improving stability, and selectivity of the sensors [26, 70, 71] as well as delivering the information needed for machine learning algorithms to accurately predict gases and mixtures [29, 72–74]. The SGP40 sensor used in this work combines the ability for modulation of the operating temperature and the advantage of a sensor array. For more information, see Section 3.1.

The extend of information gain by utilizing temperature modulation as a sensor operation can be explained best visually. In Figure 2.5 the response of the four sensing layers of the SGP40 can be seen during a full temperature cycle of temperature modulation mode (TMM) 1. The two panels a) and b) show a visual difference between the two conditions with and without CO. The fact that the difference results not only in a different magnitude of resistance (as for a fixed operating temperature), but in a fully changed pattern, explains the decreased errors obtainable from the use of machine learning for classification or regression tasks to differentiate analytes or analyte concentrations. The combination of the small sensor array made from complementary materials with temperature modulation leads to significant information gain and more features to differentiate a large variety of gas mixtures, thus opening up new possibilities for the deployment of the sensor.

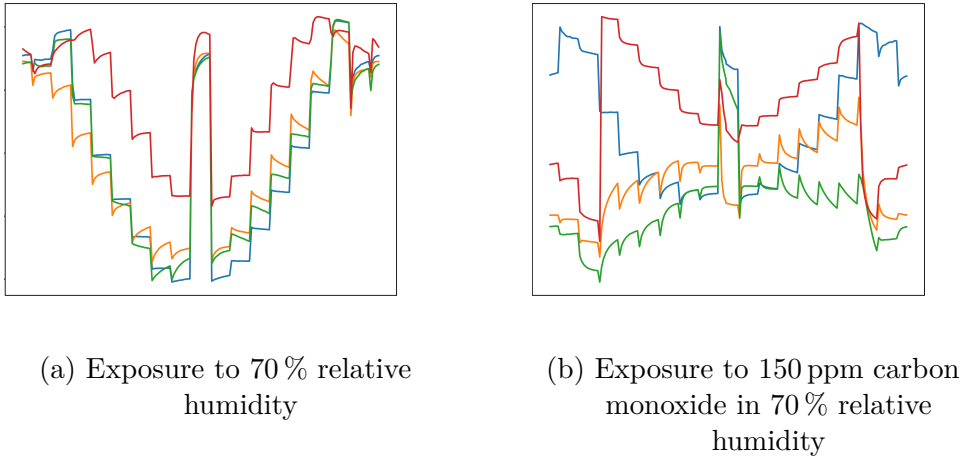


Figure 2.5: Illustration of gas and concentration specific differences in the response patterns of the four sensing units (pixels) of the SGP40 during operation in TMM 1 and a) exposure to 70 % relative humidity compared to b) 70 % relative humidity with additional 150 ppm carbon monoxide.

Electrochemical Gas Sensors

Electrochemical sensors can be classified as amperometric and potentiometric sensors. Depending on the target analyte, targeted selectivity and stability, or combination of the aforementioned, the components of the device, e.g., the materials of electrode, electrolyte, filter, and membrane are selected [75]. In the following, the fundamentals of electrochemical gas sensors are explained on the bases of [53] and [76].

Many analytes can be targeted by electrochemical cells, as the sensors can be constructed for a variety of gases using the same basic principles of operation. For instance, in the case of hydrogen detection, which is required in a multitude of applications, often under harsh conditions, the sensors need to function reliably. Temperatures can range from -30 to 1000 °C and concentrations need to be measured at a few ppm up to 100% H₂. At high temperatures, solid state materials need to be used, while low temperatures allow for liquid or polymeric electrolytes. In addition to the choice of electrolyte, the electrode material and structure, filters, membranes and operation conditions can be optimized according to the requirements and target gas. The reduction in size is a common goal across all sensing disciplines, including electrochemical sensors. This is feasible for potentiometric sensors, up to a very small size, due to the readout being voltage, which can be read out in high precision, independent of size.

Amperometric gas sensors (AGSs) on the other hand, show a decrease in current with decreasing size, due to the proportionality of the measurand to the electrode area. More recently, this can be improved with the use of suited electronics and high performance materials. The gas entering the cell through a hydrophobic membrane, to prevent leaking and the intake of dust (dependent on the manufacturer with an additional filter and/or capillary), reacts with an electrode in an oxidation or reduction. In case of AGSs, the direction of the reaction is determined by an external current. The electrical signal is produced by a current between working electrode and a counter electrode, separated by electrolyte. The measured reaction rate in amperometric electrochemical cells is limited either by gas diffusion to the sensing electrode or by the surface reaction kinetics at the electrode. If diffusion limitation is established, which is achieved by intentionally adding a physical diffusion barrier, the measured current I is proportional to the gas concentration C . Using Faraday's law of electrolysis, the current can be related to the number of molecules reacting, by Equation 2.1. Q represents the rate of gas consumption determined by the diffusion properties and geometry of the sensor, F the Faraday constant, and n the number of electrons per molecule. An additional reference electrode,

shielded from reactions, is usually provided in the device, to keep the thermodynamic potential at the sensing electrode stable, despite the electrochemical reactions happening at the surface of the electrode.

$$I = nFQC \quad (2.1)$$

Potentiometric sensors measure the potential E at a sensing electrode in comparison to the potential at a reference electrode at zero current, at thermodynamic equilibrium of chemical reactions. The electrode potential of the sensing electrode can be described using the Nernst equation:

$$E = E^\circ + \frac{RT}{nF} \ln a \quad (2.2)$$

E° in Equation 2.2 describes the standard potential of the electrode, R the universal gas constant, T is the temperature, n the number of electrons participating and a the chemical activity of the analytes, often approximated by their concentration.

2.3 Chemometrics

Chemometrics combines the disciplines of statistics with computer science and chemistry. The scientific discipline deals with large amounts of data from which, by using multivariate methods and machine learning, the chemical information is extracted [77]. A fundamental issue of any kind of data is noise. The magnitude of the signal, being the component of interest respective to background noise (which is a relative term describing virtually everything else), is called the signal-to-noise ratio (SNR) [78]. Machine learning algorithms aim to find patterns in the given data and work with the useful information. To optimize the process in finding the useful signal, pre-processing like scaling, filtering, feature engineering, or data reduction is necessary [79]. Machine learning models can be classified in unsupervised and supervised learning. Unsupervised methods, like principal component analysis (PCA), are methods in which the labels or target variables are not known. Supervised methods on the other hand use input variables $\mathbf{x}$ (also called features) from training examples with known output labels or values $\mathbf{y}$, to fit a predictive model. Using an unseen test set, the model predicts the output $\mathbf{y}$ (also called target values or labels), which can then be compared with the actual test labels or values to

obtain comparable metrics like accuracy, the coefficient of determination (R^2), or errors. Supervised methods can be further categorized in classification, with discrete classes, and regression, where a continuous range of prediction values is possible. Regression methods can usually interpolate as well as extrapolate, but the latter relies on a priori information and knowledge of the data and its behavior outside the measured or given range. In contrast to regression techniques, classification cannot predict unknown classes, meaning that all classes have to be known to the model from a balanced training in order to obtain correct predictions. A balanced training set is just as important for regression tasks to fully represent the population and deliver robust predictions [80, 81]. In this work, several regression and classification techniques are utilized, which are introduced briefly in the following sections. Pre-processing and visualization of results was conducted using mostly the Python libraries `Pandas`, `NumPy`, and `Matplotlib`. Information on the model eXtreme Gradient Boosting (XGBoost) can be found in [82, 83]. The remaining models used in this work are provided by the library `Scikit-learn` [84].

Hyperparameter Tuning

At the minimum, using a set of training data, a model's parameters can be trained to fit the training data and the accuracy or errors evaluated by the test set. Yet, many models have additional parameters, called hyperparameters, which have to be decided on when the model is initiated. To choose the best hyperparameters for the given task, the parameters have to be tested and evaluated. Usually the available data is split into three parts: training, validation and test data. The model with the first hyperparameter combination is trained, then evaluated on the validation set. This step is repeated for all hyperparameter combination and the best performing model based on the lowest error or highest accuracy on the validation set is selected. The test set is presented to the final model and the generated output and performance metrics reported, to give an estimate of the model's performance [85, 86].

Bias-Variance Tradeoff

With an increasing number of trainable parameters, a model becomes more flexible and therefore fits the training data more closely, resulting in low training error and bias. Such complex and flexible models are very sensitive towards variation in the training data, leading to overfitting and therefore poor performance and on unseen test data. This bias-variance tradeoff can be managed by various strategies: in ridge regression, the

parameter lambda or alpha regularized the model, reducing variance by discouraging large parameters and therefore simplifying the model for better generalization on the test data. Bagging techniques are used in models like random forest by averaging the predictions from multiple models with high variance trained on different subsets of the data. Boosting is used by XGBoost, learning sequentially and therefore correcting previous errors for a controlled reduction of bias or variance. Additionally, hyperparameters can be used to govern the tradeoff between complexity (variance) and simplicity (bias) [87].

The total prediction error of supervised models is composed of squared bias, variance, and a certain amount of irreducible noise, as visualized in Figure 2.6.

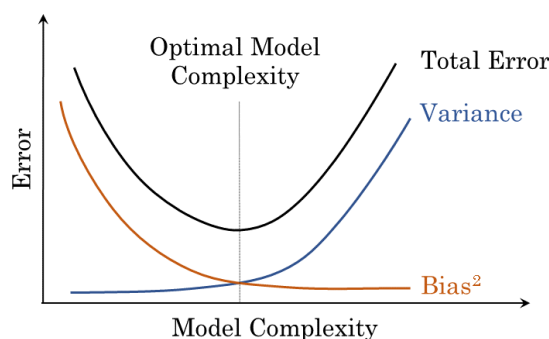


Figure 2.6: Schematic representation of the prediction error, composed of the squared bias and the variance.

Classification

As previously mentioned, classification is used when the target values can be assigned to discrete classes. The simplest form of classification is a binary classification with two labels, which, in the example of a fire detector, can be *alarm* and *no alarm*.

Linear Discriminant Analysis

The linear discriminant analysis (LDA) finds a linear combination of features to maximize the inter-class variance (between classes) while minimizing the intra-class variance (within one class) of the known classes. This way the data is separated by maximal distance between means and minimal distance of variance within classes in the new feature space, spanned by the linear discriminants resulting in a linear decision boundary. Sir Ronald Fisher developed the statistical method of Fisher's linear discriminant [88], which was later simplified to a multi-class version. Based on Fisher's

method, LDA models the distribution of the data for each class and uses Bayes' theorem to compute the conditional probability (given another event has occurred) for the new data to belong to a certain class [89, 90].

Nearest Neighbors Classification

k-nearest neighbors (k-NN) is a non-parametric or instance-based classification: it stores all training data instead of constructing an internal model with trained parameters or weights. The prediction of unknown data is made by a majority vote of the nearest neighbors (labeled training data) of each point. k is the data dependent hyperparameter, determining the number of neighbors consulted. As a rule of thumb often the square root of k is chosen as an initial guess, yet its value is dependent on the data; often an odd number to avoid a tie in their vote. The data point up for prediction is assigned to the most common class label of the k neighbors [91, 92]. As the algorithm relies on distance (mostly Euclidean), it is very sensitive to scaling.

Regression

Regression methods, as briefly touched upon in the previous sections, are used to model a correlation between the measured features and the target variables. The simplest form is univariate linear regression, for instance a calibration curve modeling the measured output of a sensor to a range of concentrations. This calibration function can be transformed in an analysis function, taking the sensors response as input to calculate the concentration of a sample.

Ridge Regression

Ridge regression is a regularized form of ordinary least squares regression. By using the L_2 term (adding the sum of weights) the regression is penalized to be more robust against overfitting and handle feature multicollinearity. This penalty can be increased or decreased with the parameter α (often lambda) [93]. The parameter α is used to manipulate the strength of the L_2 regularization of the ridge regression. Larger α results in a larger regularization, while $\alpha = 0$ is equivalent to no regularization and therefore to ordinary least squares [81, 94, 95]. Table 2.1 lists the values of α chosen in this work.

Table 2.1: Employed models and their hyperparameter search spaces.

Model	Hyperparameter	Values
Ridge Regression	α	0.001, 0.01, 0.1, 0.5, 1, 10

Random Forest Regression

Decision trees can be used for classification or regression. The structure of the tree represents the model: internal nodes are the features, branches represent the decisions (rules) and the leaf nodes the outcome, similar to the weights, input and output neurons in a neural network. Equally, decision trees are prone to overfitting.

Random forests are ensembles of multiple decision trees. Each tree is based on a random subset of samples and features building a random machine learning algorithm. By combining/averaging the predictions of all trees, the accuracy is increased and the variance reduced. This procedure is called (bootstrap aggregation or) bagging. Overfitting of single trees is less impactful with a high number of trees and samples. This method comes with the loss of interpretability, yet generally good performance [96, 97]. The number of trees and other hyperparameters were used as listed in Table 2.2. The number of trees is chosen with `n_estimators`, which can grow until reaching a maximum depth, defined by `max_depth` and the minimum number of samples before an internal node is split by `min_samples_split` [98].

Table 2.2: Employed models and their hyperparameter search spaces.

Model	Hyperparameter	Values
Random Forest	<code>n_estimators</code>	100, 200, 300
	<code>max_depth</code>	None, 10
	<code>min_samples_split</code>	2, 5, 10

XGBoost Regression

XGBoost uses boosted decision trees, where each tree is sequentially trained to approximate the negative gradient of the loss function. Instead of the averaging (bagging) used in methods like random forest, XGBoost employs an additive approach to train the learners sequentially to correct previous models/trees mistakes [99]. For

more information see [82]. The hyperparameters used for model training in this work are displayed in Table 2.3 as defined in [100]. In addition to the first two random forest parameters in Table 2.2, the `learning_rate`, `subsample` as the fraction of training samples per round and `colsample_bytree` as subsample ratio of features per tree, are trained.

Table 2.3: Employed models and their hyperparameter search spaces.

Model	Hyperparameter	Values
XGBoost	<code>n_estimators</code>	100, 200
	<code>max_depth</code>	3, 5
	<code>learning_rate</code>	0.05, 0.1
	<code>subsample</code>	0.8, 1.0
	<code>colsample_bytree</code>	0.8, 1.0

Time Series Analysis using Dynamic Time Warping

Dynamic time warping (DTW) was originally used to synchronize different speech patterns for automatic speech recognition and is now widely employed in different applications and fields. Depending on the style of music (e.g., piano version versus orchestral) or the speed of speech, the time series might not align in length, even though they contain the same information. DTW will compensate for time differences by finding the optimal, non-linear alignment (in contrast to Euclidean matching). Under certain constraints (boundary, monotonicity and step size) dynamic time warping will find a time-ordered correspondence between two time series X and Y that minimizes the cost measure c . The local cost matrix C stores the pairwise costs between all points and the warping path w is a time-ordered sequence of correspondences through this matrix. The DTW distance is the accumulated cost along the optimal path c_{w*} , defined by minimal cost. The more similar the time series, the lower the accumulated cost [101, 102].

$$\text{DTW}(X, Y) = c_{w*}(X, Y) = \min_w c_w(X, Y) \quad (2.3)$$

As DTW is sensitive to noise and magnitude of signals, often scaling is applied (here z-scaling). A warping window can be used to restrict the maximum temporal shift between the two time series that should be aligned (here 20, which was best out of None, 5, 10, 20). Documentation on the library used, can be found in [103].

2.4 Analytical Methods

Infrared Spectroscopy

Infrared spectroscopy is a common method to quantitatively and qualitatively analyze substances using infrared light. The infrared light can be divided in near-, mid- and far-infrared, out of which mid-infrared ($4000\text{--}400\text{ cm}^{-1}$) is the classical range for spectroscopic measurements.

While non-dispersive infrared spectroscopy is the standardized European method for CO detection [104], Fourier transform infrared spectroscopy (FTIR) provides a broader capability and allows for the detection of multiple components. The wavelengths of interest are measured simultaneously using an interferometer, and the resulting interferogram transformed into the frequency domain by a Fourier transform. This method is fast, accurate and has a low SNR [105].

When electromagnetic waves interact with a molecule, resonant frequencies, characteristic for the molecules structure, are absorbed. A molecule is infrared active, if its molecular dipole changes during vibration [106]. The movement of the two molecules towards and away from each other leads to harmonic oscillation, which can be described by a parabola and approximated with the harmonic oscillator. The allowed vibrational energy levels E_v can be calculated using the reduced Planck constant $\hbar$, the angular frequency ω and the vibrational quantum number v .

$$E_v = \left(v + \frac{1}{2}\right) \hbar\omega, \quad \Delta v = \pm 1 \quad (2.4)$$

The absorbed frequencies, corresponding to the excited vibrations, are expressed in wave numbers $\tilde{\nu}$. The wave numbers of two atoms (with the masses m_1 and m_2) can be calculated using the reduced mass μ , the force constant of the bond k and the speed of light c_0 .

$$\tilde{\nu} = \frac{1}{2\pi c_0} \sqrt{\frac{k}{\mu}} \quad (2.5)$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (2.6)$$

At room temperature most molecules are initially in their vibrational ground state with vibrational quantum number $v = 0$ [107]. This ground state is above the zero potential, which can be explained by the Heisenberg uncertainty principle [108]. The equidistant

energy levels of the harmonic potential can be seen in Figure 2.7 as dotted lines. At higher energy, or increasing internuclear separation, the harmonic oscillator cannot represent the vibration of the diatomic molecule anymore, because it does not allow for dissociation if a bond. This true, anharmonic motion of the molecule resembles the Morse potential (Figure 2.7), which accounts for dissociation of bonds at a finite energy and closer energy levels at higher v [107].

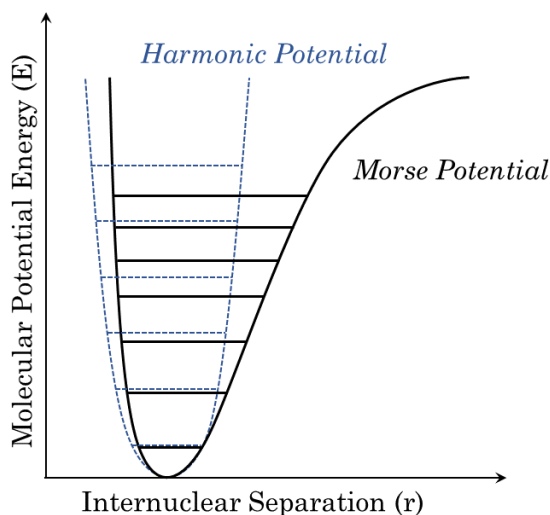


Figure 2.7: Morse potential and harmonic potential as approximations for the molecular potential energy curve of a diatomic molecule.

The ratio of the intensity detected I after passing through the sample the incident intensity I_0 is called transmittance T , which can be transformed to the absorbance A according to Equation 3.4, assuming negligible scattering and reflection [107].

$$A = -\log_{10} T = \log_{10} \left(\frac{I_0}{I} \right) \quad (2.7)$$

According to Lambert-Beer's law, the absorbance can be expressed as the product of the substance specific molar absorption coefficient ε , the concentration c and the path length within the sample l (Equation 2.8). As a result, the concentration of the analyzed molecules is proportional to the absorbance [106].

$$A = \varepsilon c l \quad (2.8)$$

Thermogravimetric Analysis

The following paragraph is a brief summary on thermogravimetric analysis, from [109]: in thermogravimetric analysis the sample mass is measured over time during temperature increase to evaluate the thermal stability of a sample. Necessary parts of the instrument are a precision balance and a programmable furnace. The mass loss (often in percentage) versus temperature curve resulting from this measurement can be interpreted regarding different changes in the sample, e.g., dehydration, vaporization, sublimation, desorption, adsorption or decomposition. Often several plateaus of constant mass and steep decreases appear, due to one or more of the aforementioned processes occurring. Thermogravimetric analysis can be run separately but is often combined with differential thermal analysis, which measured the changes in heat flux by comparing to a reference. In the differential thermogravimetric curve, peaks can occur, often directly comparable to the slope in the thermogravimetric curve. This way, information on reaction kinetics and the formation of intermediate compounds can be gained. Like in this work, the system is often coupled to a mass spectrometer.

Gas Chromatography

As described in detail in [110], many analytical techniques are non-selective and require prior sample separation. Such separation can be achieved using the technique of chromatography. In general terms, a fresh sample is injected into a mobile phase (liquid or gas), which continuously passes a stationary phase (solid or liquid). In gas chromatography, as indicated by the name, the mobile phase is gaseous, passing through a column coated with the stationary phase. A separation of the sample, moving along the column, is achieved by interactions between the analytes and the stationary phase, dependent on their chemical and physical properties. The eluate, consisting of mobile phase and analyte is then recorded by a detector. A chromatogram shows the detector response as several Gaussian curves (for the separated analytes) as a function of retention time, which is the time elapsed from sample injection to the individual peak maximum. The detector can be selected from a variety of options depending on the sample and the application. In this work, the system is coupled with a mass spectrometer.

The mobile and stationary phase as well as many other parameters like column temperature or flow rate have to be optimized to achieve maximal resolution (separation) between the analytes. The column efficiency can be expressed using the concept of

theoretical plates, describing discrete sections, where the separation takes place. Hence, the more theoretical plates per column the higher the efficiency. The relation between the number of theoretical plates N , with the height per plate H and the length L of the column is expressed in Equation 2.9, which can be directly measured using the retention time t_r and the peaks baseline width w .

$$N = \frac{L}{H} = 16 \left(\frac{t_r}{w} \right)^2 \quad (2.9)$$

While the length of the column is usually a fixed parameter, the height of a theoretical plate can be minimized. The van Deemter equation (Equation 2.10) relates the height per plate to the parameters A , B/u , and Cu .

$$H = A + \frac{B}{u} + C \cdot u \quad (2.10)$$

A describes the contribution of multiple paths available for the solute molecules to pass through the inhomogeneously packed stationary phase. For an open tubular column, the value of A , also called eddy diffusion, approaches zero. The effect of longitudinal diffusion B/u , leading to band broadening, is caused by the diffusion of solute molecules from high concentration to low concentration along the column. At lower flows, the diffusion becomes larger and dominates, while at large flows, the time for this process is limited. The mass transfer of the molecules through the stationary and mobile phase is described by Cu . By different times required for the solutes molecules to move between the interface between the phases, the solute spreads in the column. This effect is larger for large velocities, as the time for the molecules to equilibrate between mobile phase and stationary phase is even shorter. By displaying the height of plate as a function of the mobile phase velocity u , the optimum flow rate can be found as the sum of these parameters (see Figure 2.8).

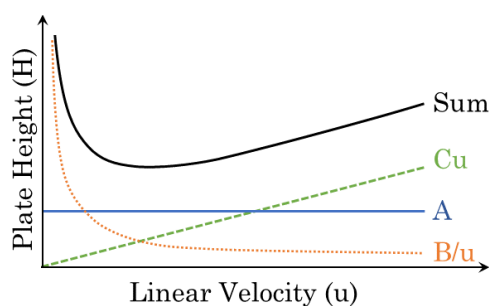


Figure 2.8: Schematic representation of the van Deemter equation.

Mass Spectrometry

This analytical technique is used for qualitative measurements like identifying unknown compounds, isotopic compositions determination and structure analysis as well as for quantitative analysis often employing a reference or standard for comparison. Fields of application include biology, environmental analysis, space exploration, quality control and forensics [111]. In a typical mass spectrometer, the following processes take place: sample molecules are ionized in the gas phase by an ion source, such as an electron beam. Due to this ionization, the molecules become (positively) charged, some under fragmentation. In the analyzer of the instrument, the ions are separated by their mass-to-charge ratio (m/z) by an electric or magnetic field [112]. According to Newton's second law, the force F acting on an ion is given by the product of its mass m and acceleration a . The motion v of ions in electric (E) and magnetic (B) fields is described by the Lorentz force with q as the electric charge [111]:

$$F = m \cdot a = q(E + v \times B) \quad (2.11)$$

Depending on the analyzer type, Equation 2.11 can be simplified. For example, in magnetic sector analyzers ions are separated by a magnetic field ($E=0$), whereas in quadrupole mass filters, separation occurs in a purely electric field ($B=0$). On a detector, the ions are registered, usually displayed in signal intensity as a function of mass-to-charge ratio. The choice of ion source, analyzers and detectors can tailor the performance to the requirements of the sample [112].

3 Material and Methods

This section describes the experimental setups, the sensors, and materials used. A special emphasis is on the newly developed ASTRA, to function as a guide for future reference. The system was built to serve as a gas mixing system (GMS) in application-close conditions, alongside acting as the test facility for the proof-of-concept and later development of a pre-ignition fire detection system for the use in space applications.

3.1 Sensors and Operation Modes

The Sensirion Gas Platform 40 (SGP40) is a digital indoor air quality sensor for volatile organic compounds (VOCs) produced by the company Sensirion in Switzerland. The sensor is characterized by low power consumption of 2.6 mA at 3.3 V* and small size ($2.33 \times 2.44 \times 0.85 \text{ mm}^3$) [61]. A publication on the predecessor SGP30, states SnO_2 with 0.1 to 5 % palladium doping [62] was employed. Yet the composition of the four sensing units on the SGP40, further referred to as pixels, is undisclosed.

The micro hotplate below the sensing material allows for fast and precise heating of the sensing materials. For this work, the sensor was operated either at a constant operating temperature of 300 °C, 350 °C, or in a TMM. The selection of temperature modulations was based on experience in comparing different modulation modes to predict concentrations of CO, H_2 , NO_2 , and toluene in relative humidity backgrounds of 5, 30 and 70 % [113].

The different temperature modulations are displayed in Figure 3.1. The standard modulation in the research group is TMM 1. Starting at 25 °C for 5 seconds, the sensing material is heated to 50 °C for 10 seconds, then 100, 150, 200, 250, 300, 250 up to 375 °C for 10 seconds respectively. After reaching the maximum temperature, the hotplate is set to 25 °C for 10 seconds before conducting the reverse of the sequence described. These

* If operated as supplied by the manufacturer, using default configuration. Dependent on the operation mode, the supply voltage can be reduced.

steps sum up to a total of 180 measurement points equal to 180 seconds, with a sampling frequency of 1 Hz. TMM 1 and TMM 2 are identical in maximum temperatures per step, but with half the length in step size, alternating between the step and the minimum temperature, which is 25 °C in case of TMM 2. TMM 3 and 5 resemble TMM 1 but with shifted minimum temperatures and a lengthier 'dip' in the middle. TMM 4 and 6 are similar to TMM 2, with higher minimum temperatures and therefore more time spend at the maximum temperature. For theoretical background and literature about the advantage of temperature modulation, see Section 2.2.

In addition to the SGP40, which was deployed for pre-ignition detection, several other sensors functioned as reference electronics for the characterization of the ASTRA, as well as temperature, humidity and pressure control. The sensors are listed in Table 3.1.

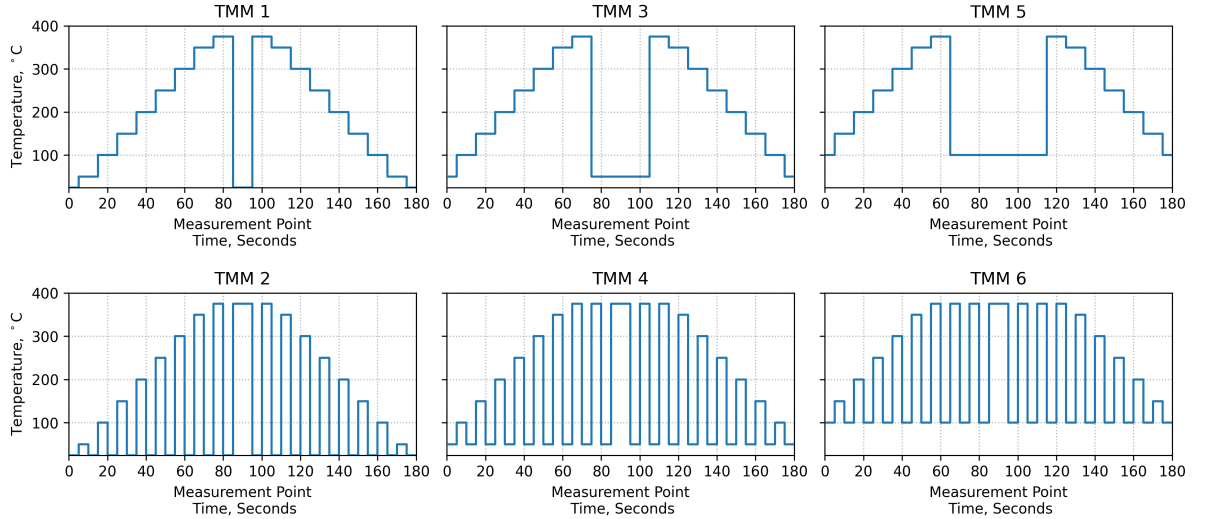


Figure 3.1: Diverse temperature modulations of the micro hotplate, heating the four sensing units in the SGP40.

Table 3.1: Sensors utilized in this work.

Sensor	Measurand	Manufacturer
HYT939	Relative Humidity, Temperature	IST AG, Switzerland
Alc/C-100	Alcohol Concentration	Membrapor AG, Switzerland
EL-USB-CO300	CO Concentration	Lascar Electronics, USA
BME280	Relative Humidity, Temperature, Pressure	Bosch Sensortec GmbH, Germany

3.2 Selected Modified Polymers

The detection system aims to detect a variety of polymers, either based on common additives or by specialization after sufficient training on the respective outgassing species. As a start, four materials were selected, known to be important and frequently used in highly restricted environments, such as the ISS.

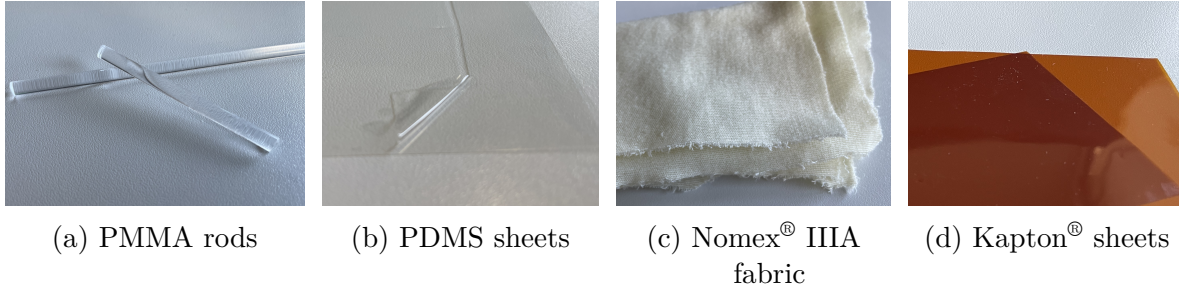


Figure 3.2: Materials used for pre-ignition measurements.

The materials chosen as representatives for modified polymers* used in space applications as displayed in Figure 3.2 are:

- a) PMMA, Vink König Deutschland GmbH, Germany
- b) PDMS, Limitless Shielding Ltd, England
- c) Nomex[®] IIIA, DuPont de Nemours, Inc., USA
- d) Kapton[®], DuPont de Nemours, Inc., USA

PMMA is the abbreviation for poly(methyl methacrylate) and PDMS stands for poly(dimethylsiloxane). While the chemical nomenclature leads to the assumption that only the raw polymer is employed, often additives are incorporated into the polymer structure. Nevertheless, the abbreviations PMMA and PDMS are used in this work to describe the materials as purchased (see Figure 3.2). Nomex[®] IIIA and Kapton[®] are both registered trademarks by the company DuPont. For readability, the registered trademark [®] and the addition IIIA will be omitted in subsequent mentions.

* In this work, the terms *Modified Polymer* and *Plastic* are used interchangeably to describe synthetic polymers modified through but not exclusively by the incorporation of additives.

The thermoplastic polymer **PMMA**, also known as Plexiglas or acrylic is used in many fields as described in detail in [114]. Some examples are windscreens, windows or viewing ports. The material is also used in solar panel covers, television screens, or laptops as well as in dental cavity fillings [115]. On the ISS, many experiments have been conducted on the flame spread of ignited PMMA in microgravity as briefly touched upon in the introduction to this work.

PDMS is utilized as adhesive, coating, or flexible insulation in electronics [116]; in skin- or haircare products, lubricants [117], flexible electronics [118, 119], or as a resin for soft-lithography [120]. The flame-resistant material **Nomex** is present in terrestrial safety gear against heat and abrasion [121], while it also finds application in different parts of space suits [122] as well as in the construction of space- and aircraft [123]. Nomex is employed as electrical insulation and mechanical protection of wire and cable bundles as well as in several equipment in aerospace [124].

Kapton is used for its thermal-insulating properties. For instance, parts of the Apollo Lunar Module, and the James Webb Space Telescope sun shield are covered with aluminized Kapton foil [125]. Additionally, Kapton tape is used in electronic manufacturing because of its electrical isolation ability. Also, it is part of the Wire Insulation Selection Guidelines of NASA [126].

3.3 Ambient-air Sensor Training and Research Apparatus

Investigations on SMOX-based sensors are often conducted during constant gas flow in GMSs. The continuous supply of fresh analyte gas, delivered almost instantaneously, leaves the sensor response unaffected by the consumption of gas and reaction products due to catalytic conversion or combustion. In real-life environments, the sensors are exposed to non-steady-state gas conditions: analytes gradually diffuse, reaction products can accumulate and concentration levels fluctuate. Additionally, the sensors' response is dependent on the type or shape of the measurement chamber [127, 128]. To simulate reality-close conditions, empty offices or laboratory rooms are frequently used and an event is generated by simple gas or liquid release [35]. The issue of manual injection, ventilation, and long equilibration times makes this approach unsuited to accumulate large amounts of data needed for evaluations with statistical value and machine learning techniques. Other environmental chambers are very complex and cost intensive, mixing synthetic or zero air with the gases, and supplying humidity coupled with temperature control [129].

The solution presented here, developed for pre-ignition fire detection as well as general indoor and outdoor air-based measurements, leverages the relatively stable temperature and humidity conditions typically found in office and laboratory environments. By using the ambient atmosphere as a base to which controlled amounts of analytes can be automatically introduced, this approach provides an efficient and cost-effective alternative to complex gas mixing and conditioning systems. This straightforward approach enables rapid air exchange within the test chamber, as ventilation and replenishment are not limited by flow rates of synthetic air cylinders or zero-air generators. Instead of attempting to simulate an atmosphere that closely mimics ambient air, the proposed approach employs ambient air directly. Humidity and temperature as well as gas composition fluctuations are of advantage to create less controlled and therefore very robust training data for machine learning applications. This setup combines the advantages of a gas mixing system and injection experiments in enclosed rooms or spaces, enabling the creation of semi-controlled test atmospheres to calibrate or test sensor systems for indoor air quality monitoring in realistic conditions. This section presents the initial ideas and constraints, operation modes, functionality, hardware, and software and is meant to double as a guide to consult when encountering problems.

Construction and Design

Based on the use cases, the system must satisfy the following boundary conditions:

- Inert materials: chemical reactions between setup materials and analyte gases injected, should be avoided.
- Heat resistance and low flammability: during tests involving heating, parts of the system will be at temperatures of up to 450 °C. For safety reasons, most materials, especially the chamber, should be inherently low-flammable.
- Interchangeable heating device: for overheating experiments within the test volume. The heat source itself must be heat- and flame-resistant and should be constructed from inert materials.
- Automated ventilation: the option to automatically replace the atmosphere inside the volume with ambient-air, for reality-close and ready-to-run training conditions.
- Analytes dosing: either as an interfering gas to test or train the robustness of the sensors, or to add gases to the test atmosphere for calibration or sensor testing.
Gases: well established and added via GMS.
Liquids: to broaden the concentration range of VOCs and allow for injection experiments.
- Large volume: to conduct spatial investigations.
- Flexible connections: to ensure adaptability for future experiments.

Several materials were evaluated as potential base materials with the conclusion, that in this early development stage, the material must be transparent. The requirement for thermal stability and resistance to VOCs like ethanol and acetone, rules out plastics like PMMA and polycarbonate. Additionally, PMMA was found to emit methyl methacrylate (MMA) by different sensors, confirmed with GC-MS. Because MMA is one of the possible trace gases to be detected from the heated samples, PMMA was ruled out as base material.

The size of the volume was set to one cubic meter to maximize experimental space while ensuring the system remains operable by a single person and mobile when equipped with castors. In cooperation with Theodor Schmid GmbH (in Tübingen, Germany) a design for the plates, made from safety glass, was realized to enclose the test

volume. The single-pane safety glass - Einscheiben-Sicherheitsglas (ESG) plates were screwed on a cuboid aluminum framework (item Industrietechnik GmbH, Germany) with cylinder head screws and perfluoroalkoxy alkane (PFA) washers, buffered with poly(tetrafluoroethylene) (PTFE) sealing in between glass and aluminum frame. The system was placed on a custom wooden workbench, equipped with six castors and making it flexible and applicable in different atmospheres at different places. The screw heads on the bottom glass plate sink into a groove, milled into the tabletop. The wooden plate was manufactured as instructed in the in-house workshop by Thilo Linke. Figure 3.3 shows a photograph of the unfinished setup.



Figure 3.3: Photograph of the test volume enclosed by plates of glass on the mobile bench. The PTFE sealing was later exchanged with a broader sealing, covering the full width of the aluminum profile.

To keep the system modular, feedthroughs from polyether ether ketone (PEEK), PTFE, and brass were designed and commissioned to the mechanical workshop in-house (Figure 3.4). The short PEEK pipe with external thread is held inside the chamber by its collar. By screwing on the brass mantle with a PTFE disc fitted in its collar, the connection can be tightened. On both sides of the glass, a flat gasket from PTFE is used as sealing and protection. The PTFE discs can be fitted with D-subminiature connectors for electronic connections, or used to pass through tubes or similar components. On the inside of the glass chamber, only wires with low outgassing insulation from polyethylene tetrafluoroethylene (ETFE) (TE Connectivity, Ireland) are used, as included in the Wire Insulation Selection Guidelines by NASA [126].

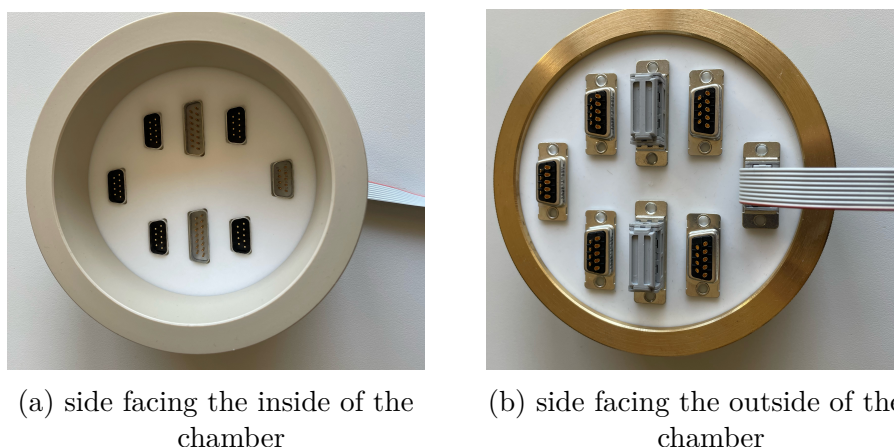


Figure 3.4: Assembled feedthroughs with D-subminiature connectors to connect electronic components using flat ribbon cables outside the system and ETFE cables inside (not connected here).

Depending on the experimental requirements, the system can be equipped with a slow-moving fan (22 revolutions per minute), operated by a small motor, to create uniform distribution of gases in the atmosphere. Aside from the heating source, operated during the material overheating experiments by a separate `Python` script, three main processes are controlled using custom software (see *Measurement Software*): ventilating the system, analyte dosing, and the evaporation of liquids. For the execution of these processes, the ASTRA is equipped with a ventilation system, consisting of metal tubing and electrical shutters (Belimo Holding AG, Switzerland). On one side a straight fan TWINLINEA (Vetus, Denmark) is drawing in fresh air when the ventilation process is started and the shutters open. This ventilation can be used to clean the

system after each gas mixture was created and measured. The air exchange of the system is controlled by a Raspberry Pi (Raspberry Pi Foundation, England), connected to a relay board. The relays turn on or off the ventilators and open or close both shutters for a variable time. The desired test atmosphere can be created by dosing different analytes in the system. Two types of analyte injections are implemented: gas dosing and liquid dosing. A schematic of the setup with the two dosing mechanisms and the heat source for the investigation of material outgassing is displayed in Figure 3.5.

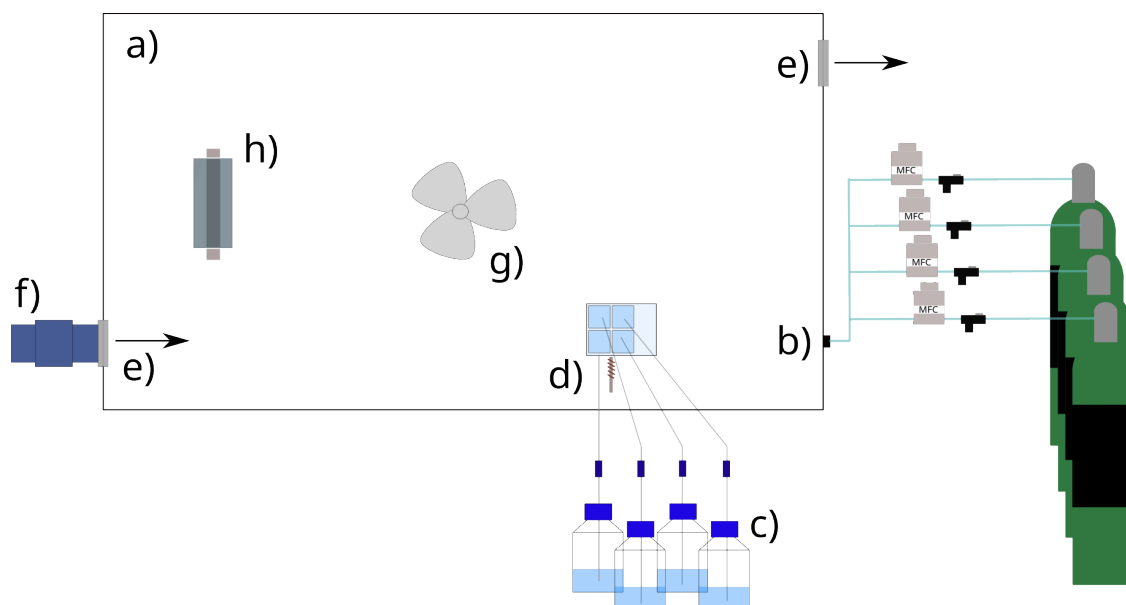


Figure 3.5: Schematic representation of the ASTRA setup: a) glass walls; b) inlet connecting to gas mixing system with mass flow controllers and pressurized gas bottles; c) aqueous solutions of liquid analytes in flasks with PTFE tubes and micro pumps, connecting to the vaporizer d) consisting of a PTFE plate with four basins mounted on aluminum plate, heated by induction; e) automatic shutters; f) in-line-blower; g) slow-moving fan; h) custom tube furnace for material overheating studies.

Gases

Gas mixtures can be dosed using a GMS, similar to the GMS in Section 3.4 but without humidifier, attached to one of three built-in 6 mm Swagelok connectors. The analyte gas bottle is attached to a magnetic valve and a mass flow controller (MFC), the control of which is achieved with the software QBPY (see *Measurement Software*) communicating with a socket-server operating the gas mixing system. The calculation of concentration is done by integrating the actual opening of the respective MFC over time. The flow

rate $F(S_i)$ for every instance i is calculated for the actual setpoint S_i , send from the MFC, and its measured maximum flow and offset. The actual concentration c_{actual} is then computed using trapezoidal integration, according to Equation 3.1.

$$c_{\text{actual}} = \left(\sum_{i=1}^n \Delta t_i \cdot \frac{F(S_i) + F(S_{i+1})}{2} \right) \cdot \frac{c_b}{V} \quad (3.1)$$

Here, $\Delta t_i = t_{i+1} - t_i$ is the time interval in seconds, c_b is the bottle concentration, and V is the chamber volume.

Liquids

Another socket-server, responsible for liquid dosing, communicates with the following hardware: an ESP32 (Espressif Systems, China) connected to a micropump driver mp6-QuadKEY, attached to up to four micropumps (Bartels Mikrotechnik, Germany). When liquid dosing is initiated, the desired amount of liquid is transferred from a stock solution through PFA tubing into a PTFE basin. The weighting and heating are achieved by the vaporizer (Figure 3.6): a PTFE plate with four basins is attached to an aluminum plate and a loadcell (Sparkfun Electronics, USA). A coil attached to a low voltage induction heater (Shenzhen Hailege Technology Co., Ltd., China) is surrounding a stainless-steel screw in the middle of the aluminum plate. To achieve more accurate mass readings, the scale, to which the basin is permanently attached to, is regularly calibrated using a reference, to remove zero offset and gain error.

The full process of liquid dosing and heating takes place as follows: first the empty PTFE plate is weighed by the attached scale using a loadcell amplifier HX711 (Sparkfun Electronics, USA). Up to four pre-mixed aqueous solutions can be dosed from the stock solutions through PFA tubes into one of the four basins of the PTFE plate, inside the test chamber. The needed mass of the solution to obtain the desired concentration is pre-calculated using Equation 3.2.

Every second, the scale weighs the content of the basins and the result is logged. The system automatically stops the pumping when the target mass is reached. After five seconds sleep time, the scale is weighing* the solution to include drops, occurring slightly after the initial pump-stop, and a second analyte is ready to be dosed in the same fashion, for a total of four times (four basins), if desired.

* All weights recorded for zero scaling, calibration and analyte mass determination represent the average of 50 measurements.

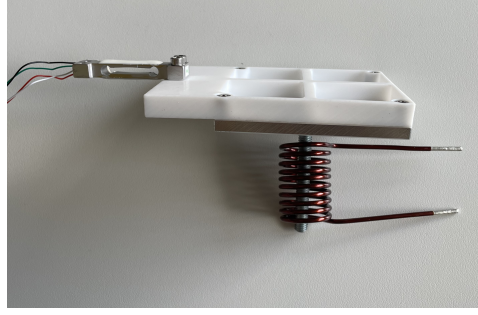


Figure 3.6: Vaporizer consisting of an aluminum plate, with a stainless-steel screw attached to a PTFE plate with four basins for liquids. The basin is heated with induction, generated from the coil. The amount of liquid is weighed by the loadcell (top left).

Because of the possible overshoot of liquid, the concentrations can be larger than anticipated. To be able to report the exact concentration, they are automatically calculated for each analyte using the actual dosed mass and the known concentration of the stock solution as described in Equation 3.3. Then the induction heater heats the metal plate underneath the PTFE plate for a pre-set duration, causing the solution to evaporate. The start and end times of the process are recorded, as well as the measured mass.

$$m_{\text{calc}} = \frac{c_{\text{input}} \cdot M_{\text{analyte}} \cdot n_{\text{chamber}}}{c_{\text{stock}}} \quad (3.2)$$

$$c_{\text{actual}} = \frac{n_{\text{analyte}}}{n_{\text{chamber}}} = \frac{c_{\text{stock}} \cdot m_{\text{actual}}}{M_{\text{analyte}} \cdot n_{\text{chamber}}} \quad (3.3)$$

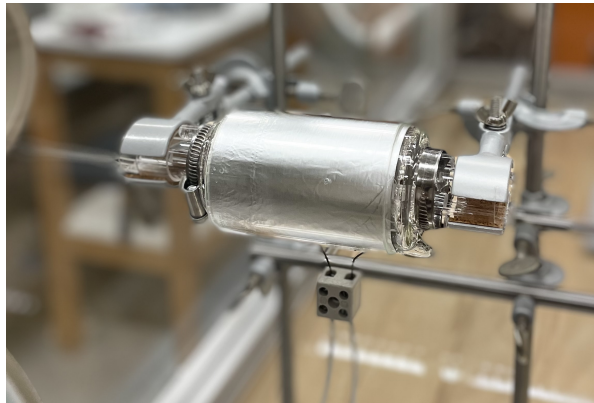
Here, m_{calc} is the mass calculated to reach the designated gas-phase concentration, c_{input} is the desired input concentration (e.g., ppm, ppb, or %), M_{analyte} is the molar mass of the analyte in g/mol, and $n_{\text{chamber}} = \frac{V_{\text{chamber}}}{V_{\text{molar}}}$ is the number of moles in the chamber at standard conditions. V_{chamber} is the volume of the chamber, while $V_{\text{molar}} = 24.464 \text{ L/mol}$ is the molar volume of an ideal gas at 25 °C and 1 atm. Additionally, c_{stock} denotes the concentration of the stock solution, c_{actual} is the actual gas-phase concentration resulting from the dosed liquid, n_{analyte} represents the number of moles of analyte introduced, and m_{actual} is the actual mass of liquid dosed in grams.

The two dosing mechanisms can be combined and several gases and liquids dosed. The mixture is then held for a pre-defined dwell-time before system ventilation begins,

completely exchanging the air in the system, allowing for a new mixture to be generated. All processes can be adapted to the desired duration.

Heat Source

In order to heat materials in a controlled manner, without adding to the outgassing from the device itself, a custom tube furnace was developed in cooperation with Haile Solomon in the scope of his admission paper [130]. The glass ware was produced by Thomas Nieß in the in-house glass workshop. The furnace consists of an inner glass tube (200 mm length, 21 mm inner diameter), with Kanthal[®] wire wrapped around. Using notched quartz glass sticks, the wire is kept in place. To capture the heat in the inner volume and protect the user from the electrical current, the Kanthal[®] wire is shielded with a vacuumed glass tube (120 mm length, 40 mm inner diameter), mantled in aluminum foil, and an outer glass tube (100 mm length, 60.5 mm inner diameter). The furnace is depicted in Figure 3.7.



(a) tube furnace in the test volume of the ASTRA



(b) tube furnace without outer aluminum and glass mantle

Figure 3.7: Custom tube furnace for overheating experiments, made from glass, Kanthal[®] wire, and aluminum foil, at different stages of assembly.

Five quartz glass boats were manufactured, which can be inserted in the middle of the oven, loaded with the respective material. For the measurement, the materials PMMA, PDMS, Nomex, and Kapton were cut into small pieces (PMMA: 0.2–3 mm discs cut from rod, rest: 0.5–1.5 cm length and width) and approximately 200 mg placed into small glass boats. Each material was assigned an individual boat and one was reserved as a blank. For information on the materials see *Selected Modified Polymers*. The temperature is controlled by the Reflow Master Pro (RMP) (Unexpected Maker Shop, Australia) measuring the temperature of two K-type thermocouples (B+B Thermo-Technik GmbH, Germany) switching a solid-state relay (on/off), connected to a 24 V, 5 A power supply heating up the Kanthal® wire. Figure 3.8 visualizes the connections and sources to control the processes of the air exchange, evaporation of liquids, and operation of the tube furnace.

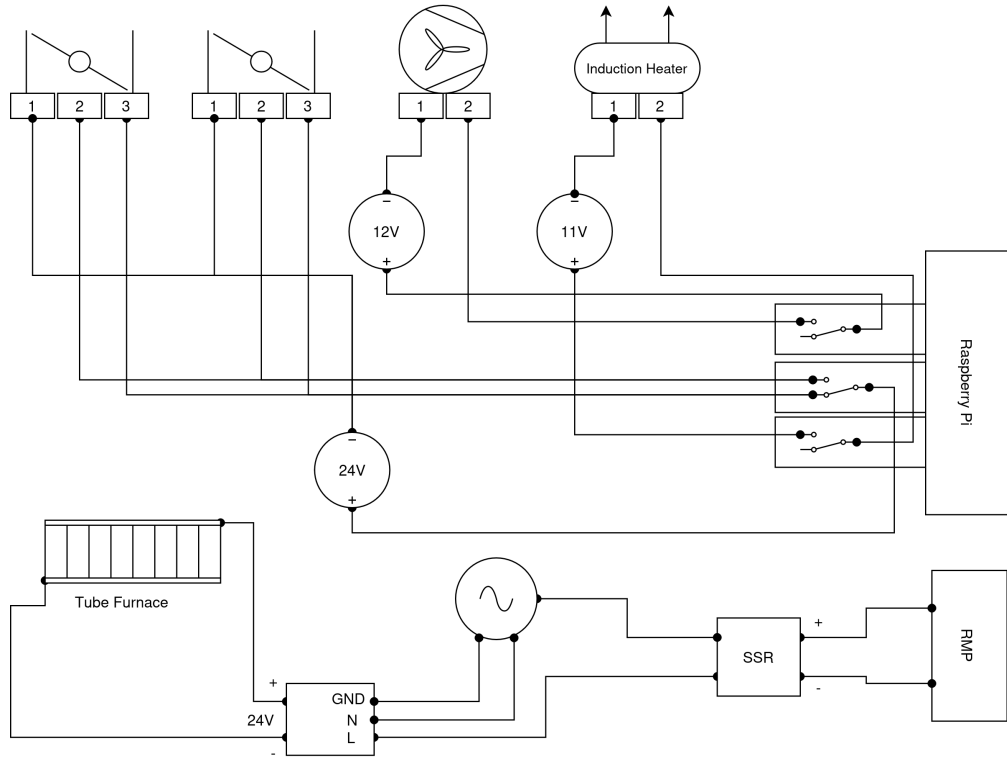


Figure 3.8: Simplified wiring diagram for the basic components of the ASTRA. The upper diagram visualizes the connections of the two shutters and the in-line-blower for the systems ventilation as well as the induction heater controlled by the Raspberry Pi. The lower diagram shows the wiring of the tube furnace to the RMP.

Measurement Software

In order to achieve the requirement of automatic operation, a software was developed. In the early development stage, with ongoing changes and improvements necessary, a custom `Python` script served this purpose, allowing for fast and easy adaptations. In later stages, with partly defined hardware, the code was implemented into the existing framework `PyGUI` [131] under the name `QBPY` by Luca Völkl during his master's thesis [132]. Maintenance activities and additional hard- and software implementations were executed by the author, facilitating subsequent experimental modifications. `GPT-5/GPT-4o` (OpenAI) was utilized to support debugging and code development. The software communicates with three main instances:

- The socket server for gas dosing, controlling the attached GMS with its magnetic valves and MFCs.
- The socket server for liquid dosing, forming communication to the ESP32, starting the process of liquid dosing, reading out, and reporting back the mass obtained with the loadcell and amplifier.
- A web service hosted by the Raspberry Pi, operating the relays to control the air exchange and the evaporation of dosed liquids via HTTP-requests (Hypertext Transfer Protocol).

The flowchart of the software `QBPY` is displayed in Figure 3.9 and explained in detail in the following.

when executed, the graphical user interface (GUI) gives the option to press a `start`-button and supply an excel file containing the desired gas mixtures (concentration per analyte), heating, ventilation, and equilibration duration for the measurement. Configurations like gas bottle concentration, characteristics of the MFCs, molecular mass of the analytes, and concentrations of stock solutions connected to the micro pumps have to be supplied. Using the first input-line, the software follows the fixed sequence and execute functions/threads. When the first thread is finished, the second thread is started and so forth. If there is no input supplied for a specific task in the input file, it is skipped. By leaving specific operations empty (or set to zero), the fixed sequence can be adjusted, otherwise the system will proceed in the following order.

Purge: the relays connected to the Raspberry Pi are toggled, opening the shutters and activating the ventilation of the system. The air in the system is exchanged by surrounding air for the time set in the input file. Once the time has elapsed, the relays are toggled again, closing the shutters and turning off the ventilation.

Dose gases: via the corresponding socket-server, the respective MFCs are opened fully, the output is logged and by integrating over the flow and time, the concentration is calculated (Equation 3.1). As soon as 95 % is reached, the respective MFC is closed by 50 %. Once the desired concentration is reached, the MFC closes fully.

Purge gas inlet: the tubing connecting the gas bottles to the measurement chamber is flushed with synthetic air. The duration of inlet-flushing can be set in the input file to make sure the consecutive mixture does not contain left over amounts of gas from the tubing, and the current gas mixture contains exactly the amount aimed for without loss from gas still in the tubes.

Dose liquids: the socket-server for liquid dosing communicates with the respective hardware and liquids are dosed from the stock solution. The calculated mass is dosed and the actual mass is reported back and then converted to an actual concentration.

Evaporate: for the time stated in the input file, the induction heater is activated, heating the metal plate attached to the basins. The respective relay is toggled by the Raspberry Pi once to start, and once to end the process.

Equilibrate: for the time set as equilibrium time, the system is in a static condition. Only the slow-moving fan is in motion. This allows for the gases to mix within the system and for the sensor data to be acquired.

Switch line: after the equilibration task is done, the count of excel lines is increased by one, and the variable containing the information on the threads status is updated to finished.

The process is repeated if the timer callback, activated every 10 seconds, recognizes that `switch line` was called and no thread is running. The new excel line is read and

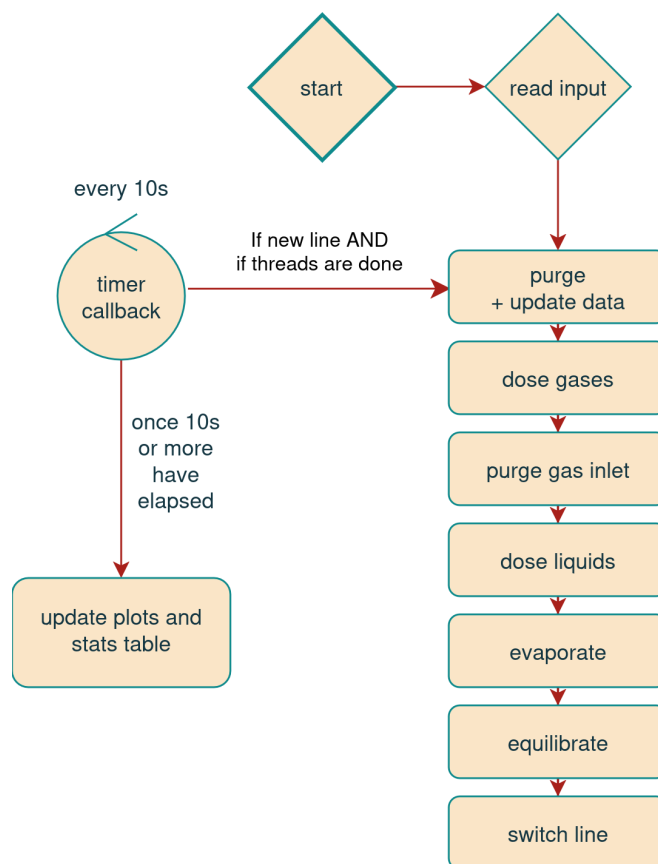


Figure 3.9: Software flowchart, displaying the basic functions to operate the apparatus.

the process starts again with **purge**. Every 10 seconds, the incoming data of the scale, MFC feedback, or timestamps and status of relays (ventilation, shutters and induction heater) is saved to a local file, and uploaded to an in-house **gilgamesh** database using **PostgreSQL** [133]. Additionally, all instances supplied in the input excel sheet are recorded (e.g., concentration of stock solution, pressurized gas bottles, MFC calibration data, etc.).

The last instance to be controlled is the RMP, not currently included in **QBPy**, because of the future objective of switching the heat source. The RMP and tube furnace are therefore operated independently but automated by a **Python** script. By simply selecting the material inserted in the tube furnace, a pre-defined (but adjustable) temperature program is loaded. The process is initiated with optional subsequent exchange of the air in the ASTRA. The set and actual temperature is logged in the database **gilgamesh** and can later be consulted.

Sensor Grid and Gas Source Arrangement

To build the CSG for gas source localization, 32 sensors of type SGP40 were arranged in the ASTRA volume and fixed on a metal framework. The sensors were operated at constant 350 °C. The distribution of the sensors is visualized in Figure 3.10, with the three positions (marked with the numbers 1, 2, and 3) the tube furnace was placed in. The furnace was positioned approximately 21 cm above the base plate and approximately 26 cm from the side walls in position 1 and 3, while placed in the middle of the setup when in position 2.

The nomenclature of the sensors is XYZ , according to the axis in Figure 3.10. X describes the sensors locations on the YZ -plane and can either be a , b , a' , or b' . Y describes the height (1, 2, or 3), the sensors were mounted at, and Z the orientation on the horizontal axis in numbers ranging from 1 to 4. The sensors with $X=a'$, or b' were not perfectly aligned on Z , but shifted approximately 8 cm towards the short plane of the volume (in Z -direction) as displayed in the schematic. To improve visual clarity and because the difference is negligibly compared to the scale of the setup, they are labeled in the same fashion.

The sensors could not be coherently oriented in the exact same way, because of fixed and rigid cable-to-breakout-board connection, but the direction of all sensors on the Z -axis was towards the maximum. A photograph of the sensor network within the chamber is supplied in Figure 3.11. During the localization measurements, the slow-moving fan was removed from the system.

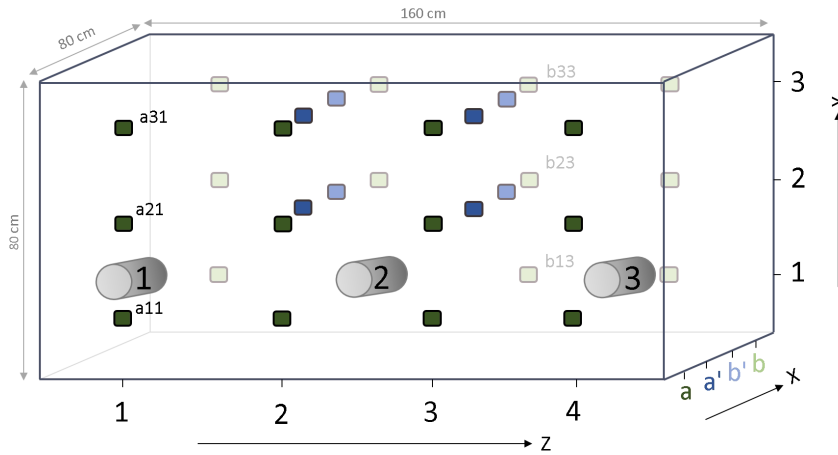


Figure 3.10: Schematic displaying the arrangement of the sensors in the ASTRA and positions of the tube furnace. Reprinted from [134](^{*} see next page).

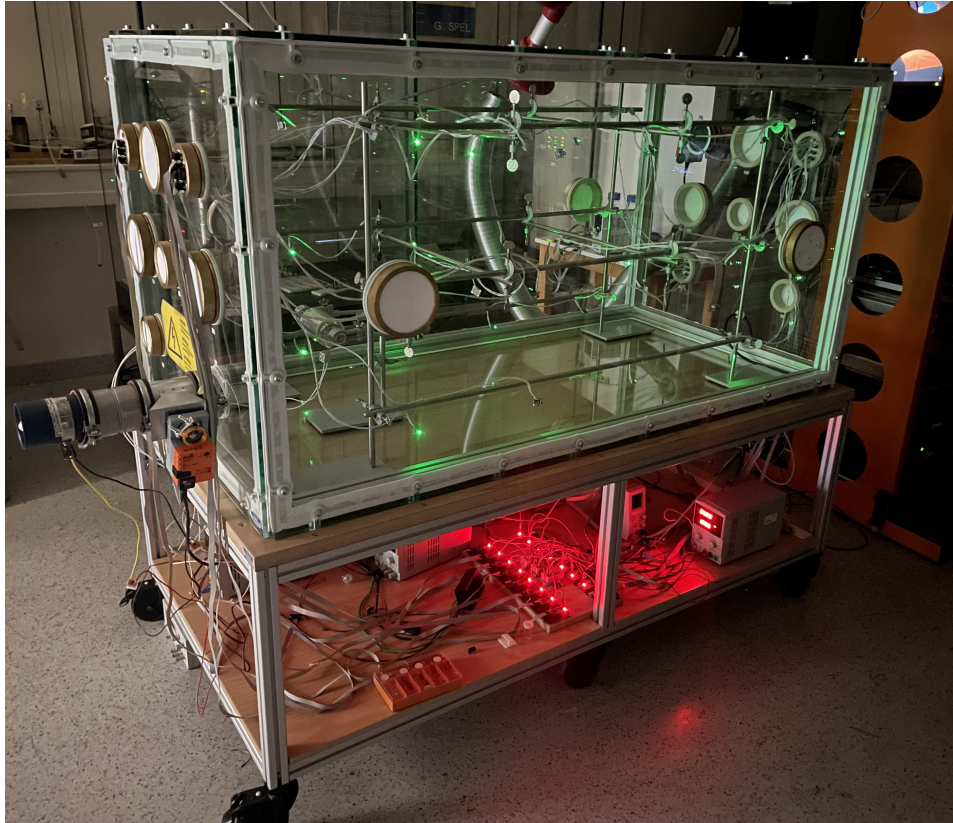


Figure 3.11: Photograph of the sensors arranged within the ASTRA. The individual sensors can be identified from the green LEDs. Reprinted from [134]*.

* Reprinted from L. Schynowski, F. Meyer, U. Weimar, N. Barsan, Exploring pre-ignition source localization using a 3D network of semiconducting metal oxide gas sensors, *Sensors and Actuators B: Chemical*, 2026, 467: 140442, © 2026 The Author(s), licensed under CC-BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

3.4 Standard Systems

Several systems or devices were used as reference or for characterization. These systems are described in the following as standard systems – in contrast to the ASTRA, developed as part of this work.

Gas Mixing System

In the field of gas sensing and gas measurement technology, GMSs are state of the art. The basic components are MFCs, magnetic valves and pressurized gas bottles. The connecting tubes and parts are either from stainless-steel (Swagelok, USA) or polymers like PTFE or PFA. A schematic of a standard GMS setup is shown in Figure 3.12. A carrier gas, usually synthetic air or nitrogen, is supplied from one of the pressurized gas bottles (Westfalen AG, Germany). By adding a combination of analytes, a gas mixture can be created. The analytes consist of bottles containing pre-concentrated gases in synthetic air or nitrogen. Humidified air is created by leading synthetic air through a humidifier. The carrier gas flow is adjusted in a fashion that the combined flow stays at the pre-defined rate. The MFCs (Bronkhorst, The Netherlands or Sensirion, Switzerland) and magnetic valves are computer controlled by PyMFC [131].

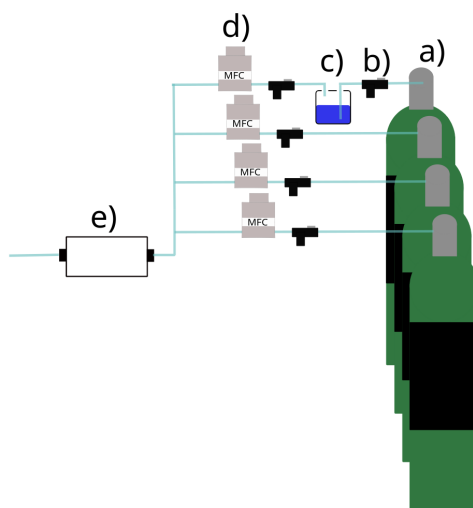


Figure 3.12: Schematic representation of a GMS for measurements in dynamic condition. a) gas bottles with attached pressure reducers connected via PFA tubing and Swagelok connectors to b) magnetic valves; c) humidifier; d) MFCs, and e) sensor chamber made from PTFE.

Before commissioning, after any changes to the setup, the mass flow controllers are calibrated using the bidirectional mass flow meter ASF1400 (Sensirion, Switzerland). The gas mixture is presented to the sensors in the PTFE sensor chamber and then led to the exhaust. A reference sensor module containing one SGP40 (Sensirion AG, Switzerland) and the humidity sensor HYT939 (Innovative Sensor Technology IST AG, Switzerland) is used to monitor the GMS' functionality.

The setup enables dynamic and rapid changes in conditions within seconds, making it ideal for investigating time sensitive sensor characteristics such as response and recovery time. The resulting gas composition and the associated changes differ significantly from real-world environments, where slow continuous changes by diffusion, natural convection, or minimal buoyancy effects are determining the movement of gas molecules in the atmosphere.

Gas Phase Transmission Spectroscopy

To validate the calculations for concentration in the ASTRA, gas phase transmission spectroscopy was conducted. The calibration was done by attaching a GMS to a long-path gas cell (PIKE Technologies, Inc., USA) of 2.4m optical path length, 100 ml volume and a 37.5×4 mm KBr window (the cell replaces the sensor chamber in Figure 3.12). The measurement was conducted using the FTIR spectrometer Vertex 70v (Bruker, USA), equipped with a mercury cadmium telluride (MCT) detector (Bruker, USA), cooled by liquid nitrogen. During the measurements, the spectrometer department was evacuated and the sample department kept at atmospheric pressure. The spectra were recorded with a resolution of 0.5 cm^{-1} and 32 scans collected with a scanner velocity of 10 kHz, using the detector and the software OPUS (Bruker, USA). The gas for the calibration was supplied by a standard GMS as previously described.

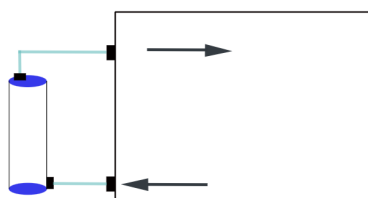


Figure 3.13: Schematic of the setup for sampling dosed concentrations from the ASTRA. The air is pumped from the system through the gas cell in a closed loop.

The sampling from the ASTRA was carried out by connecting the inlet and outlet of the gas cell via built-in Swagelok connectors (see Figure 3.13). The connectors are located on the opposite side of the gas inlet and vaporizer (see Figure 3.5). The air was drawn through both volumes continuously using four micropumps connected to the micropump driver mp6-QuadKEY (Bartels Mikrotechnik, Germany). The spectrum of interest was divided through a reference spectrum and the resulting ratio transformed to an absorbance spectrum according to Olinger and Griffiths [135]:

$$\text{Absorbance} = -\log \frac{\text{spectrum of the analyte}}{\text{spectrum of the reference}} \quad (3.4)$$

The reference spectra were always taken in the same condition as the sample. For instance, the reference spectra for the ASTRA were acquired during the equilibrium phase, as it would be for an analyte sample, but without prior gas dosing.

To cover the concentration range of 1–200 ppm CO, two different gas bottles had to be utilized and therefore two separate measurements recorded. The sampling from the ASTRA was timed to be during the equilibrium state, for 15 minutes. The pumps are able to transfer 6 ml/min, which adds up to 24 ml/min. Given the gas cell volume of 100 ml, 15 minutes of pump operation flushing 360 ml of air through the cell, should suffice.

Thermogravimetric Analysis Coupled with Mass Spectrometry

As a method for investigating the thermal-driven mass loss, thermogravimetric analysis was performed on the modified polymers. It was coupled with mass spectrometry to gain insight in the species exiting the material due to the rise of temperature. The measurements were conducted and evaluated at the University of Bremen by Malte Schalk. The measurement was run using a Netzsch STA 449 F3 Jupiter and Netzsch QMS 403 Aëolos Quadro (Netzsch-Gruppe, Germany). 10 mg of sample was placed into Al₂O₃ crucibles and heated by the built-in furnace. The gas was transferred to the mass spectrometer through a heated line.

A gas mixture containing 19.7 % of oxygen was delivered continuously from pressurized gas bottles (Westfalen AG, Germany) to the instrument. The gas flow was created from 37 ml/min of argon, 14 ml/min of oxygen and 20 ml/min protective flow. For each sample, 30 minutes in isothermal mode at room temperature was initiated to remove gas contaminants brought to the system during sample preparation. The samples were

then heated to 800 °C at a rate of 10 K/min and subsequently cooled back to room temperature. A differential scanning calorimetry sample carrier was used to measure the sample and an empty crucible as reference. Additionally, a blank measurement without a sample was conducted to serve as baseline/background correction.

Gas Chromatography Coupled with Mass Spectrometry

A measurement series using GC-MS was conducted by Björn Spranglewski and Dr. Daniel Buchner at the Center for Applied Geoscience (ZAG), using an Agilent 7890A and Agilent 5975C (Agilent Technologies, USA). The system was operated using 1 ml/min of helium as carrier gas in split-less mode at an injector temperature of 220 °C and 1.1487 bars, with a Restek-VMS column (60 m × 250 µm × 1.4 µm, Restek Corporation, USA). The column oven was programmed to 40 °C for 30 minutes, then increased to 220 °C at a rate of 5 K/min, held for 2 minutes and then further increased to 240 °C at 20 K/min, where the temperature was held for another 9 minutes. The total run time adds up to 68 minutes, with an equilibration time of 0.5 minutes.

The transfer line was set to 250 °C and the detection carried out using electron ionization in scan mode, in a mass range of 20–350 m/z, without solvent delay. The temperature of the source was at 230 °C and the quadrupole temperature at 150 °C.

The data was obtained using the software **Agilent ChemStation** and potential analytes matched using the National Institute of Standards and Technology (NIST) mass spectral library with the software **NIST MS Search**.

4 ASTRA - Exploratory Characterization

This chapter is intended to demonstrate the operational performance and explore the characteristics of the ASTRA* rather than to provide statistically conclusive results, as this highly modular system is intended to be frequently modified and adapted to the experimental requirements. During all measurements shown in the following, the slow rotating fan in the middle of the setup was in operation.

As described in the previous sections, two dosing mechanisms are available, titled **liquid dosing** and **gas dosing**. With gas dosing as the common way of introducing gases to a system (using an attached GMS) and liquid dosing as a way to cost-efficiently broaden the spectrum of a gas concentrations of VOCs available in pressurized bottles. Carbon monoxide was chosen exemplarily as a representative **gas** that could be added during sensor training. It is visible in infrared spectra and can be measured using electrochemical sensors, making it an ideal candidate for tests and calibration. As a representative for a **liquid** to be dosed, EtOH was selected. It can be mixed with water in any ratio and measured with the same techniques.

Both gases are found on the ISS, however in different concentrations: CO was measured in concentrations of 1–2.2 ppm [136, 137], for the characterization of the system, the gas was dosed in larger concentrations to ensure success of the measurements.

During operation in 2023 and 2024 ethanol was measured in concentrations of approximately 0.5–5.6 ppm aboard the ISS [136, 137]. The concentration range of ethanol for the system characterization was extended to 8 ppm, as it should readily be detected in this quantity.

* Ambient-air Sensor Training and Research Apparatus

Under normal conditions, both analytes are not expected to occur in substantial concentrations indoors. Nevertheless, CO can originate from heating or combustion appliances, cigarette smoke or vehicle emissions, entering a room through ventilation systems or open windows [138]. EtOH evaporates from cleaning products [139], disinfectants [140], emerges during cooking activities [141], or is emitted from human occupants [142]. The biggest source of any analytes being drawn into the ASTRA, arises from nearby measurements and their exhaust. Especially bottle swaps along with the required ventilation of analytes from the tubing and pressure reducers of adjacent setups into surrounding air. Even if small, this influence should be kept in mind as well as the changing concentration of other gases originating from ongoing work in the occupied lab space.

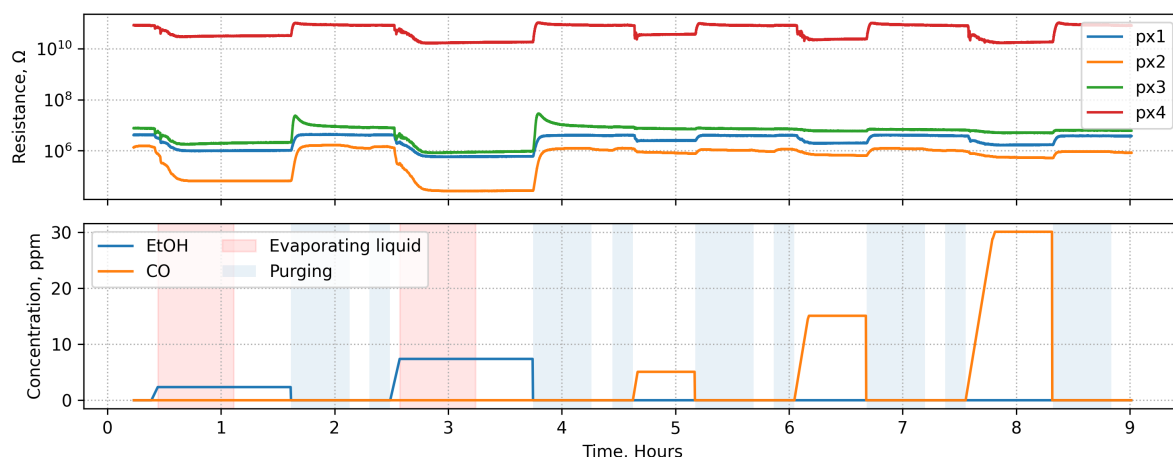


Figure 4.1: Different modes of operation in the ASTRA. Top: exemplary measurement showing the response of the pixels on the SGP40 in a typical sequence. Bottom: set concentrations of the analytes carbon monoxide and ethanol.

Using the SGP40, an exemplary measurement was recorded, as displayed in Figure 4.1. The different modes of operation (gas dosing, liquid dosing, equilibrium phase, and purging of the volume) are clearly visible in the pixels' responses. Overall, the four pixels show similarities in their resistance curves, although at different magnitudes. In the subplot at the bottom, the state of the system is shown as well as the set concentration: ethanol in a blue line, CO in orange. The purge of the air is visualized in light blue and heating of the vaporizer in light red shading. Equilibration periods are deliberately not indicated, as there is no active process taking place.

The visualization of the set concentrations is identical for both analytes. An increase in

concentration is displayed until the desired amount is reached. A plateau indicates the unchanged state of the system (equilibrium) before the next purge is started and the set concentration drops immediately to zero.

Starting with a purge, the air was vented for 10 minutes (not explicitly marked in the bottom plot). During this time the pixels were at their baseline. When the ethanol-solution was dosed for the first time, the pixels started to react, which is visible as a drop-in response for all of the four. Immediately after the dosing of liquid was completed, the induction heater was activated to evaporate the liquid. Already after a fraction of the heating period, the ethanol seems to have evaporated based on the stability of the resistance curves. Once the full 40-minute heating phase was completed, the system was set to equilibration state for the same duration. The pixels show to be unaffected by that. During the purge thereafter, a strong increase in resistance can be observed. Pixel 3 and pixel 4 show an overshoot above baseline level, before approaching a constant value. For the subsequent 10 minutes, the system was in the equilibration state: only the slow-moving fan inside the glass chamber was in motion, everything else was turned off. For pixel 2, the short time in equilibrium mode is visible as a small decrease in response.

Generally, the baseline in the system is at slightly lower resistance for all of the four pixels, when compared to during the purge or with open shutters. This leads to the conclusion that the air in the system is more reducing, due to VOCs from sealing or other components*. While pixel 2, generally showing the strongest response to VOCs, reacts to a change in the system, no such indication was detectable for pixel 1, 3, and 4. The outlined sequence was repeated for another iteration of EtOH in larger concentration, starting with 10 minutes of purging. The four pixels show identical trends.

CO was dosed from a pressurized gas bottle through the GMS, traceable as a sudden decrease in the resistance of all four pixels after the purge of the system (approximately 4.5 hours into the measurement). From the visualization of the resistance, the response is still slightly decreasing when the next purge was initiated, followed by the short equilibrium phase, again only reflected by pixel 2 of the SGP40.

* No measurable changes between inside and outside the system could be clearly attributed to a change in VOC levels, ozone concentration, or other.

To be aware of any changes in pressure, four pressure sensors were implemented. Two were placed inside and two outside of the volume of the ASTRA. They showed a change of 1 mbar between any operational state and the purge of the system, which is negligible compared to the natural atmospheric pressure fluctuations of approximately 30 mbar for the sensors inside and outside of the system in the same scale. From the sensor readings, relative humidity fluctuates roughly between 15 % and 60 % and temperature is usually in the range of 20–27 °C, depending on seasonal changes and weather condition.

4.1 Actual Concentrations

With the newly developed system, the accuracy of dosing needed to be verified. The concentration error (Error) in ppm is calculated using Equation 4.1 and the relative error (RE) with Equation 4.2. $c_{\text{predicted}}$ is the concentration calculated using the custom-made software and c_{actual} the concentration measured by the respective instrument or device. The mean absolute errors (MAEs) and mean relative errors (MREs), as well as the standard deviations, are calculated using the absolute errors to represent the deviation from the aimed value.

$$\text{Error} = c_{\text{actual}} - c_{\text{predicted}} \quad (4.1)$$

$$\text{RE} = \frac{c_{\text{actual}} - c_{\text{predicted}}}{c_{\text{actual}}} \cdot 100 \% \quad (4.2)$$

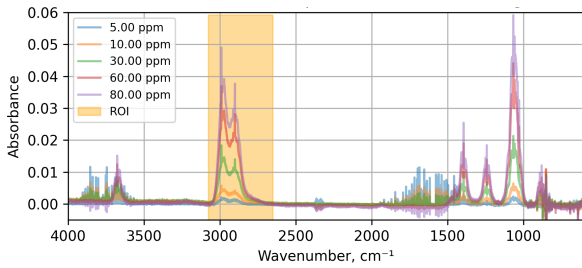
Infrared Spectroscopy

To ensure that the concentration dosed matches the concentration calculated, a measurement series was conducted using infrared spectroscopy.

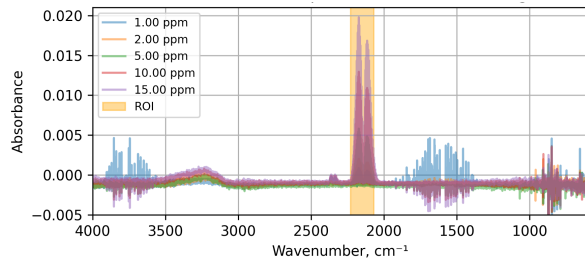
For a quantitative evaluation of unknown concentrations, first a calibration had to be obtained. Using a GMS, different concentrations of CO and EtOH were delivered to the gas cell and measured by the instrument. For detailed information on the instrument and setup see *Gas Phase Transmission Spectroscopy*. The absorbance spectra of the calibration series with the empirically selected region of interest (ROI) for EtOH and CO are displayed in Figure 4.2.

On the basis of the acquired data for both analytes, calibration curves were calculated using the area under the curve (AUC) and the peak maximum in the corresponding

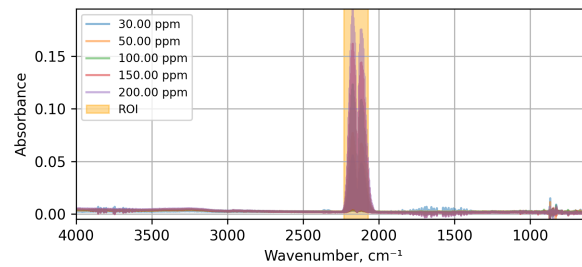
region the analyte is active, against the concentration. Therefore, the ROI was selected ($2070\text{--}2230\text{ cm}^{-1}$ for CO, and $2650\text{--}3070\text{ cm}^{-1}$ for EtOH), a baseline correction applied, and the two metrics calculated using `numpy` `trapz` and `max`.



(a) absorbance spectra of EtOH



(b) absorbance spectra of CO – small concentration range



(c) absorbance spectra of CO – large concentration range

Figure 4.2: Absorbance spectra of ethanol in a) and carbon monoxide in b) and c). Obtained using a standard gas mixing system.

Gas Dosing

In theory, according to the law of Beer-Lambert (Equation 2.8), a linear fit should represent the relationship between concentration and absorbance. Nevertheless, the measurements of the two concentration ranges of CO show a mismatch. To compensate for the experimental deviation, presumably due to variations in the bottle concentration (Westfalen gives a 2% error), a quartic (4th-degree-polynomial) fit was applied. Using this empirical correction, the R^2 values could be improved to 0.998 for the peak maximum and AUC respectively. Figure 9.1 in the *Appendix* shows the data obtained and the two fits as well as the corresponding residuals.

Four concentrations of CO were sampled (5, 15, 30, and 150 ppm), repeated three times. During the extraction of the features from the absorbance spectra, large noise was observed, as depicted in Figure 4.3. The H_2O region and the ROI are superimposed. Furthermore, the peak at 2090 cm^{-1} , originating from H_2O , represents the peak maximum in the ROI for the set concentrations of 5 ppm and 15 ppm. For that reason, the second largest peak had to be consulted for the low-concentration spectra. In case of the spectra of 30 ppm and 150 ppm, the CO signals are large enough for the peak maximum to stay uncorrected.

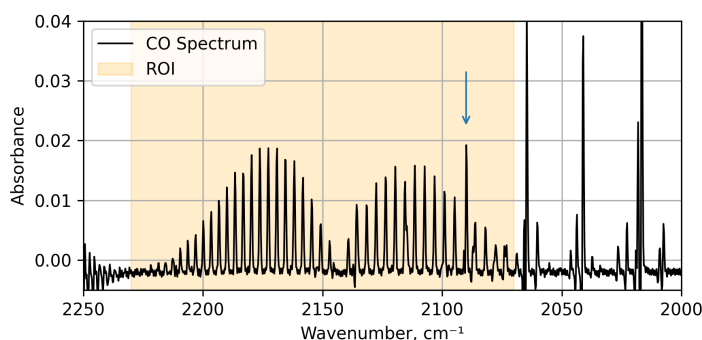


Figure 4.3: Absorbance spectra of 15.2 ppm predicted carbon monoxide concentration according to the ASTRA software, before baseline correction.

Table 4.1 lists the MREs and MAEs of the peak maximum for concentrations greater than or equal to 30 ppm and the second peak maximum for concentrations below. When comparing the AUC with the peak maximum, the latter shows slightly lower values. For both features, increasing concentration leads to a decrease in MRE. The absolute errors stay more consistent, with the exception of the values for 151 ppm, which had to be dosed with a gas bottle of higher concentration. As the concentration is dependent on

many factors (which will be discussed later on), it is not possible to conclude on a trend from this selection of data.

The parity plot of the actual against the predicted concentration of CO (Figure 4.4), shows an alignment along the ideal line for both, AUC and the peak maximum. Actual concentrations at the predicted 151 ppm are in $\pm 10\%$, while most of the lower concentrations exceed that border. The lower concentrations of approximately 5 and 15 ppm vary stronger when using the feature peak maximum.

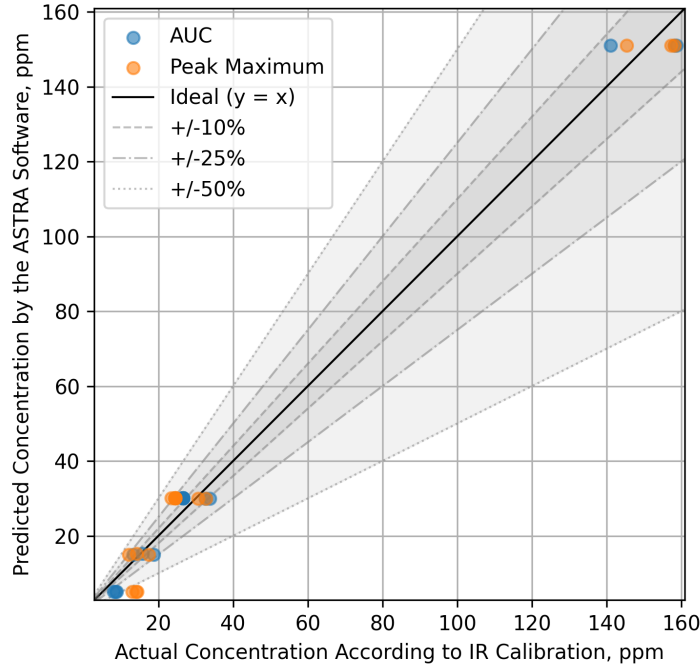


Figure 4.4: Parity plot of carbon monoxide showing predicted concentrations from QBPY and actual concentrations from the infrared spectrometer calibrations.

Table 4.1: Mean errors for calculated concentrations of CO, supplied by the gas dosing mechanism of the ASTRA, using the infrared spectrometer calibrations.

Mean Predicted Concentration, ppm	MRE AUC, %	MRE Peak, %	MAE AUC, ppm	MAE Peak, ppm
5.07	40.19 ± 3.31	21.69 ± 6.83	3.42 ± 0.45	1.44 ± 0.59
15.07	12.27 ± 8.17	12.51 ± 3.48	2.02 ± 1.60	1.77 ± 0.32
30.03	10.82 ± 2.75	8.45 ± 6.61	3.30 ± 0.66	2.42 ± 1.70
151.00	5.48 ± 1.34	4.13 ± 0.37	8.28 ± 1.43	6.36 ± 0.80

Liquid Dosing

The calibration curve of both AUC and peak maximum yielded a R^2 value of 1.00 for EtOH, using a linear fit. After transforming the calibration into an analysis function, concentrations were calculated from peak maximum and AUC. A visual representation of the six calculated (predicted) concentrations, logged by the software QbPy (Equation 3.3) against the resulting measured (actual) concentration, obtained by gas phase spectroscopy, is supplied in Figure 4.6. Error boundaries were added as a visual aid. The parity plot of EtOH shows all concentrations obtained with the peak maximum having high errors. The concentration, according to the infrared calibration measurements, is about five to ten times higher than the predicted concentrations. The AUC shows a better alignment with the ideal trend line, but again with the actual concentration higher than the predicted one. The concentrations sampled from the volume of the ASTRA are listed in Table 4.2 for liquid dosing of ethanol, with their corresponding mean relative errors and mean absolute errors for the AUC, as well as the peak maximum.

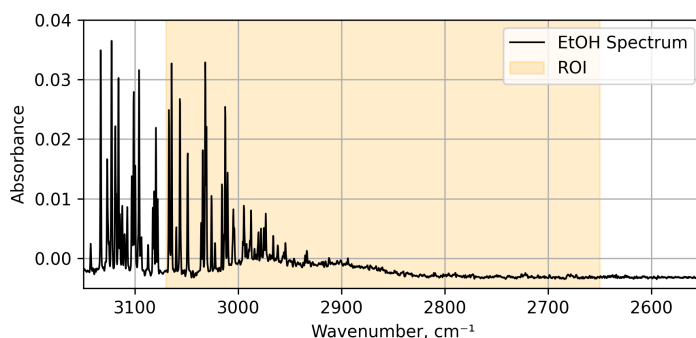


Figure 4.5: Absorbance spectra of 8.4 ppm ethanol obtained from the ASTRA by liquid dosing before baseline correction.

The resulting errors clearly indicate that the metric peak maximum with the MREs above 92% and 83% and MAEs more than 32 ppm, contains a systematic error. In contrast, the MREs and MAEs for using the feature AUC seem more realistic, while still showing a directional error. The AUC errors are larger for smaller concentration of EtOH and suggest by their magnitude, that concentrations of single digit ppm or lower might either be dosed incorrectly or measured with insufficient SNR. For this reason, the sampling and measurement of additional, lower EtOH concentrations was omitted. In order to identify the reason for the high errors in peak maxima, a spectrum of the

highest concentration sampled (8.4 ppm) is visualized, representatively in Figure 4.5. Interferences could be caused by H_2O and CO_2 , judged by their typical wavenumbers. Based on the structure, the interference likely occurs due to changes in relative humidity [143–146]. The overlap of different regions and comparably low absorbance in the ROI explain the high errors, their variance, and direction. In the spectra using a standard gas mixing system (Figure 4.2), the background was more constant by the nature of the instrument, therefore avoiding this issue.

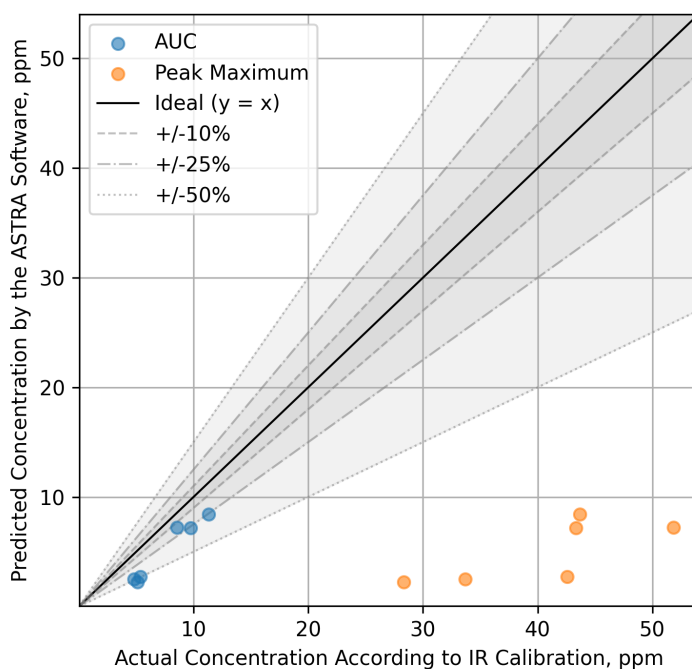


Figure 4.6: Parity plot of liquid dosed ethanol showing predicted concentrations from QBPY and actual concentrations from the infrared spectrometer calibrations.

Table 4.2: Mean errors for calculated concentrations of EtOH, supplied by the liquid dosing mechanism of the ASTRA, using the infrared spectrometer calibrations.

Mean Predicted Concentration, ppm	MRE AUC, %	MRE Peak, %	MAE AUC, ppm	MAE Peak, ppm
2.49	51.06 ± 4.28	92.74 ± 0.80	2.60 ± 0.28	32.35 ± 6.95
7.60	22.64 ± 6.09	83.43 ± 2.65	2.28 ± 0.84	38.68 ± 5.13

Overall, the quantitative analysis of CO concentrations using gas phase infrared spectroscopy could deliver a first insight of the systems performance. The MAEs

for EtOH are below 2.7 ppm, using the metric AUC for all concentrations sampled. For CO, the peak maximum feature outperformed the AUC with MAEs ranging from 1.4 to 6.4 ppm across the concentrations explored. In conclusion, initial information on concentration errors was gained, but the method poses difficulties because of the superimposed regions. In addition, the conduction of ventilation, manual sampling, the transfer, and measurement in the infrared spectrometer are too time-consuming to be conducted on a regular basis.

Electrochemical Gas Sensors

For an automated data collection, gas sensors are generally well-suited devices. On-line measurement is possible, and the sampling time at 15 minutes into equilibrium can be selected during evaluation without data loss. Electrochemical gas sensors (also referred to as e-cells) were chosen, as they are selective, easy to operate and of low cost [147]. As the sensors selected have different properties (e.g., resolution, stability or cross-selectivity), the following data was acquired within three months of sensor delivery. As the data sampling was done fully automated, less supervision and interferences were necessary. Therefore, the concentration ranges were adjusted: carbon monoxide was measured in a finer resolution, but not above 60 ppm, to ensure safety in the laboratory space (5, 10, 15, 20, 25, 30, 40, 50, and 60 ppm). Ethanol dosing was set to 0.5, 2, 4, and 8 ppm. Again, each concentration was dosed and sampled three times.

Gas Dosing

To evaluate the system during operation and compare the concentrations of CO obtained with infrared spectroscopy to another instrument, the EL-USB-CO300 was programmed to measure every 10 seconds and placed inside the glass chamber on the opposite side of the gas inlet. The concentration, 15 minutes into the equilibrium state, is displayed against the concentration calculated from the ASTRA's software as a parity plot, in Figure 4.7. A trend is visible concerning the magnitude and direction of the errors: lower measured concentrations seem to be estimated (predicted) too high while higher concentrations seem to be estimated too low. As a result, the errors and relative errors of low concentrations (5 and 10 ppm) are negative, while for high concentrations they are positive. The corresponding mean errors are reported in Table 4.3: the highest MRE was calculated for 5.06 ppm and the lowest for 60.04 ppm. Except for the lowest

concentration, all MREs are below 10%. The mean absolute errors are consistently below 2.5 ppm, with standard deviations of 0.01–1.04 ppm.

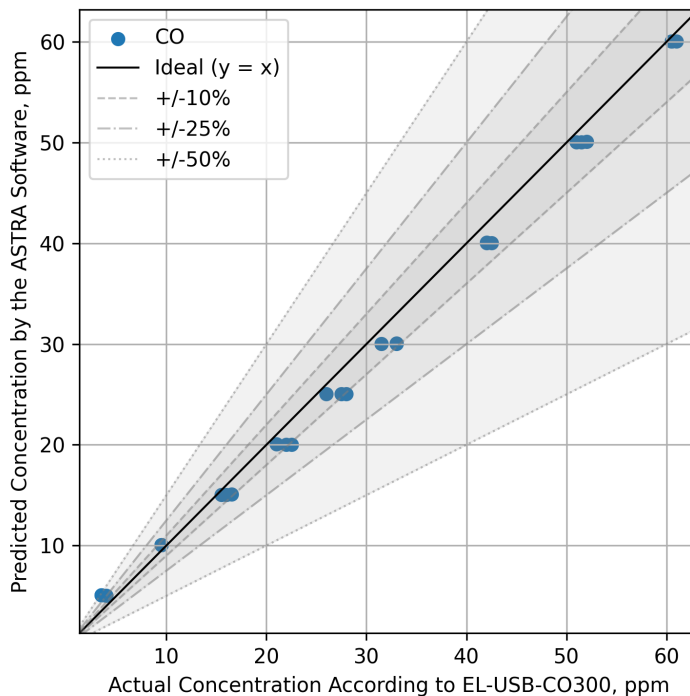


Figure 4.7: Parity plot of carbon monoxide showing predicted concentrations from QBPy and actual concentrations from the EL-USB-CO300.

Table 4.3: Mean errors for calculated concentrations of CO, supplied by the gas dosing mechanism of the ASTRA, using the EL-USB-CO300.

Mean Predicted Concentration, ppm	MRE, %	MAE, ppm
5.06	38.62 ± 10.71	1.40 ± 0.30
10.07	5.97 ± 0.11	0.57 ± 0.01
15.05	5.89 ± 2.88	0.95 ± 0.49
20.04	8.13 ± 0.77	1.79 ± 0.77
25.05	7.72 ± 3.59	2.12 ± 1.04
30.05	7.50 ± 2.47	2.45 ± 0.85
40.05	5.03 ± 0.66	2.12 ± 0.30
50.06	2.79 ± 0.91	1.44 ± 0.48
60.04	1.03 ± 0.45	0.62 ± 0.28

Liquid Dosing

In the ethanol measurement the Alc/C-100 was used, measuring every 500 ms. Figure 4.8 depicts the parity plot, comparing the calculated ethanol concentration with the measured. Low deviation from the ideal relation is observable, especially for the concentrations on the upper end. In the concentration range of ethanol, the MAEs are at 0.27 ppm or below (Table 4.4). The magnitude of the MREs and their standard deviations for ethanol decrease with increasing concentration from 15.43 to 1.85 %.

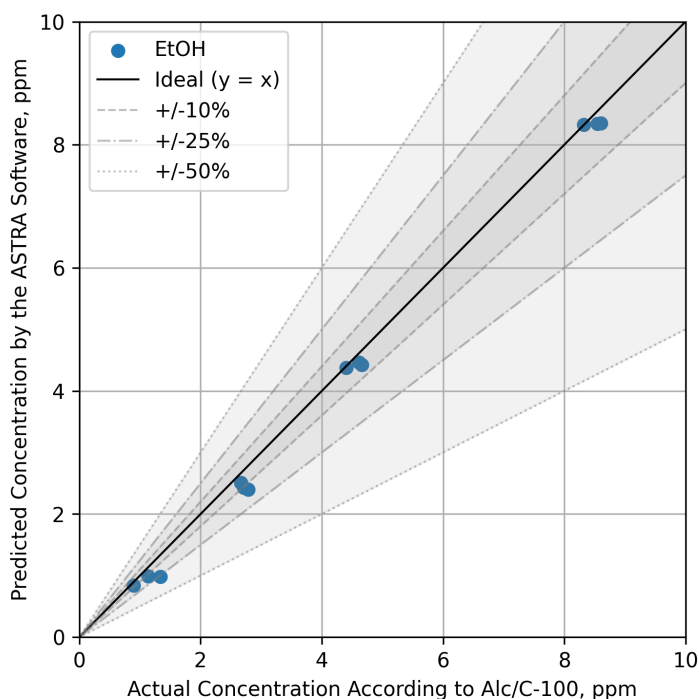


Figure 4.8: Parity plot of ethanol showing predicted concentrations from QBPy and actual concentrations from the Alc/C-100.

Table 4.4: Mean errors for calculated concentrations of EtOH, supplied by the liquid dosing mechanism of the ASTRA, using the Alc/C-100.

Mean Predicted Concentration, ppm	MRE, %	MAE, ppm
0.94	15.43 ± 10.11	0.19 ± 0.15
2.45	10.01 ± 3.97	0.27 ± 0.11
4.42	2.91 ± 2.26	0.13 ± 0.11
8.34	1.85 ± 1.49	0.16 ± 0.13

When comparing the errors of both methods for the matching concentrations in Figure 4.9, the e-cell (green) clearly yields lower errors than both features obtained from gas phase spectroscopy in the ethanol measurements.

The MAE, obtained with the infrared spectrometer, shows lowest values using the e-cell for CO, except at 30 ppm. The lowest MRE for carbon monoxide was calculated for the peak maximum at 5 ppm, while the electrochemical sensor showed lower errors for 15 ppm and slightly lower and less deviated errors for 30 ppm. Interestingly the errors at 15 ppm CO are lower than the remaining concentrations, as measured by the electrochemical gas sensor.

Despite the overall better performance of the e-cells, the resolution of the EL-USB-CO300 of 0.5 ppm limits the measurements in lower concentration ranges, as observable by the comparably high MRE in Table 4.3, with large standard deviation for 5.06 ppm. The manufacturer of the electrochemical gas sensor Alc/C-100 reports a resolution of 0.05 ppm, yet regular zero-point calibration seems necessary to maintain a stable baseline.

Nevertheless, given the benefit of the sensors measuring on-line, compared to complex and error-prone procedure of sampling manually and placing the cell in the infrared spectrometer, in addition to the reported superimposed regions, the method of error assessment using electrochemical gas sensors is clearly preferred.

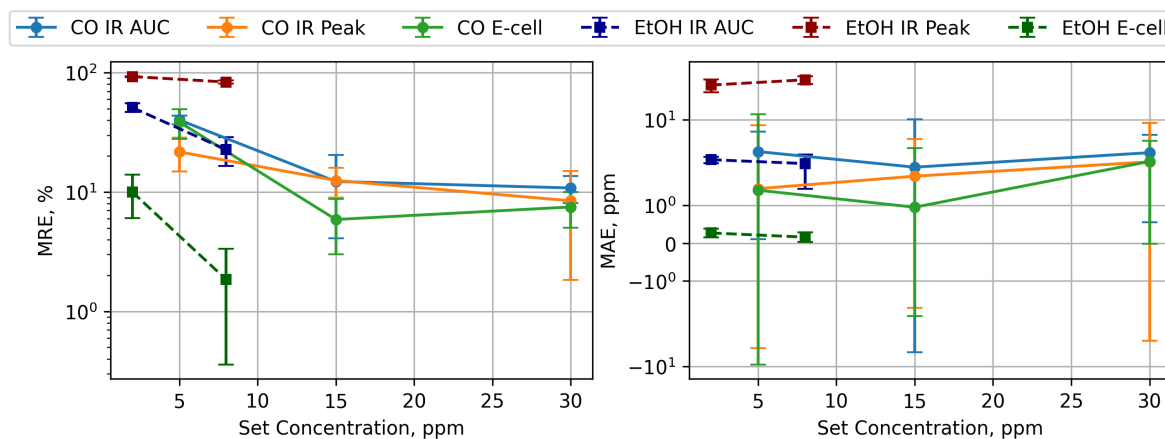


Figure 4.9: Relative and absolute errors for calculated concentrations of EtOH and CO comparing the results obtained with the electrochemical gas sensors and the infrared spectrometer.

4.2 Concentration Dependence on Time

Due to the fact that the ASTRA, with all its different materials and connections through the volume, cannot contain a concentration indefinitely, the time passing after a gas being dosed has a large impact on the current concentration. Two processes are taking place at the same time: the mixing of gas inside the volume, governed by diffusion and forced convection (by the slow rotating fan), and its escape through small unsealed openings. In the previous Section 4.1, the sampling time was empirically set to 15 minutes into equilibrium, for the objective of insight on initial accuracy and repeatability. Nevertheless, in order to predict the concentration evolution of a given gas in the system, the full process has to be monitored and the true maximum concentration tracked.

Gas Dosing

After the gas is being dosed, some time is required for it to mix with the ambient air in the system. A rotating fan in the middle of the setup is usually in operation to speed up the process. Figure 4.10 shows the mean concentration and standard deviation of three measurements per CO concentration, respectively. The measurements were recorded with the EL-USB-CO300 and are displayed against the time passed after the dosing stopped. The RE of the mean concentration per subplot is included in absolute values in grey.

For 5 ppm, a strong increase is visible before the concentration virtually plateaus for most of the remaining duration. The RE reflects that by a first drastic, then steady decrease. For 10 ppm the trend remains the same, in contrast to all following concentrations, which are reaching a maximum, then declining. In that case, the RE drops to a value close to zero, then increases to a maximum (coherent with the concentration exceeding the predicted concentration), decreases again to close to zero, before reflecting the decline of concentration by a steady increase. Interestingly, the plateau of both, concentration and error, seem shorter for higher concentrations. Before attempting to explain the phenomenon, it can be deduced from Figure 4.10, that the 15 minutes mark (after gas dosing is stopped) is an acceptable time to sample close to the plateau or maximum concentration and compare the methods for the concentrations discussed, even though a time adjusted to the concentration might improve accuracy and precision of results in the future, especially for concentrations above 40 ppm.

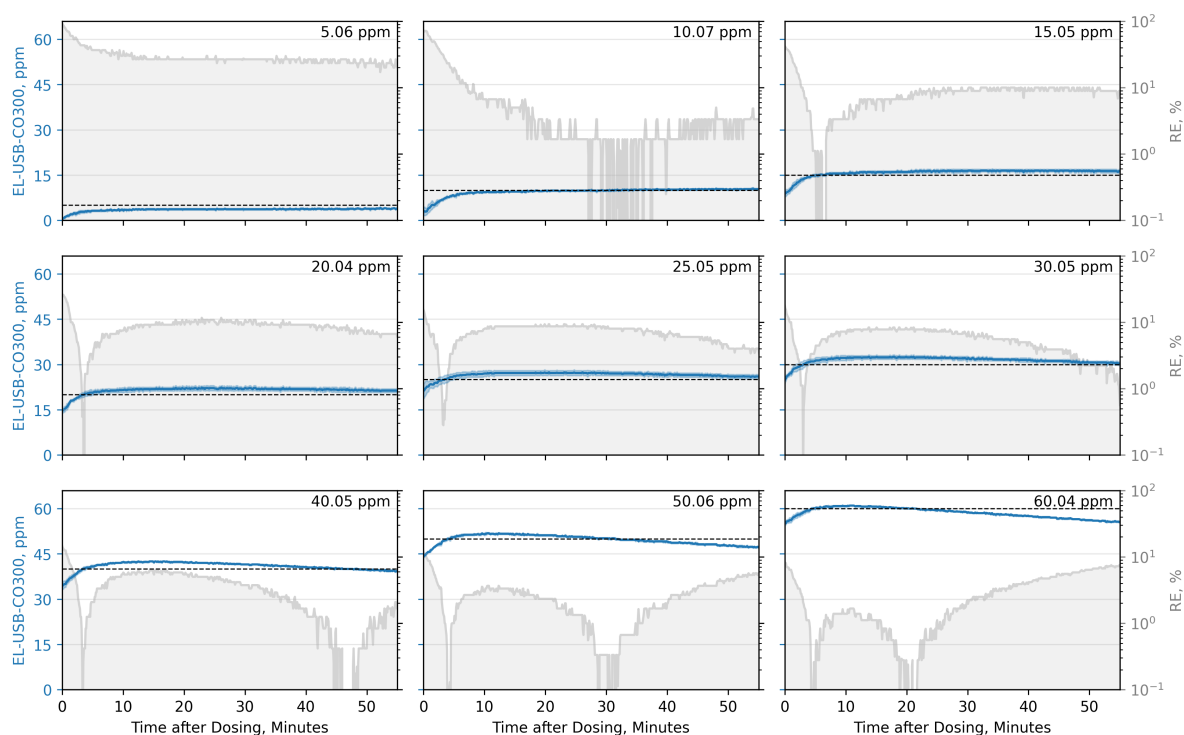


Figure 4.10: Mean concentration and standard deviation against the time after CO dosing was stopped. On the secondary y-axis, the absolute of the corresponding relative error is displayed. The mean predicted concentration by the software of the ASTRA is displayed in the upper right per panel and as a horizontal dashed line.

In the top panel of Figure 4.11, the measurements are displayed in one single plot with the peak maximum of the mean concentration marked by a dot. The sampling time of 15 minutes into equilibrium is displayed as a dashed line. This sampling time was closest to the concentration maximum of set 40.05 ppm CO. The time required for the lower concentrations (e.g., 10.07 ppm and 5.06 ppm) to reach their maximum is longer, compared to the high concentrations. Linked to that, by the end of the time window, the error still decreases between 15.05 ppm–30.05 ppm, while increasing for the concentrations above. The maximum in response, calculated for the mean at set 10.05 ppm, is located at the end of the timescale, limited by the purge that was initiated after 60 minutes.

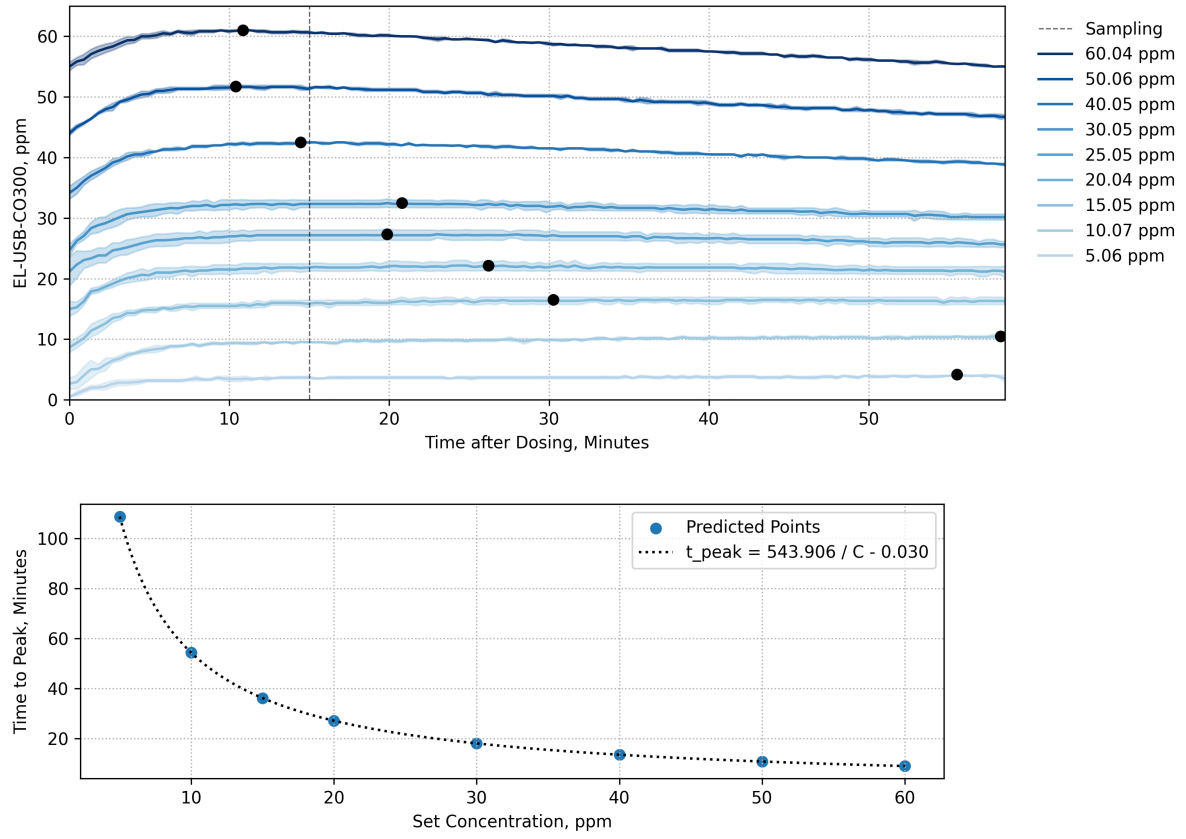


Figure 4.11: Dependence of CO concentration on time. Top panel: mean concentration and standard deviation, grouped and labeled by set concentration of repeated measurements against time, after dosing was completed. Black dots mark the maximum concentrations for the first time reached. Bottom panel: analysis function derived from the upper panel, describing the time required after dosing to reach the maximum.

The relationship between concentration and time elapsed until the reach of the maximum concentration can be fitted using a hyperbolic fit, with C as the concentration set to be dosed. The resulting analysis function, defining the sampling time for a given set concentration, is displayed in bottom panel of Figure 4.11 as t_{peak} .

The time required for the concentration to mix within the volume and reach the sensor located far from the inlet, is in competition with the process of concentration decrease through small unsealed openings. Aside from the influences of the slow-moving fan, according to Fick's first law of diffusion, the diffusion flux is proportional to the concentration gradient [107]: if the introduction of a gas creates a large difference in concentration, the resulting high gradient leads to fast diffusion. As the system

approached a more uniform concentration, the gradient decreases and diffusion slows down. The same principle applies for the diffusion through holes, yet the concentration outside of the system can be approximated as constant. Additionally, larger gas concentrations take more time to be fully dosed in the system (from the same gas bottle). Therefore, the time required for the gases to reach the maximum, is highly dependent on the bottle concentration. In this measurement series, it took approximately 31.5 minutes to dose 60 ppm, while only 2.4 minutes to dose 5 ppm of CO. By applying this time correction, the peak maxima cluster around 35 minutes after dose-start, with 5 and 10 ppm appearing as outliers. Given the sensor's resolution of 0.5 ppm, the low-concentration measurements and their corresponding maxima should be treated with caution.

Liquid Dosing

For the liquid dosing mechanism, the mean concentration, measured by the Alc/C-100, is visualized in Figure 4.12 as a function of the time. In the top right corner per subplot, the mean concentration by QBP_y is reported.

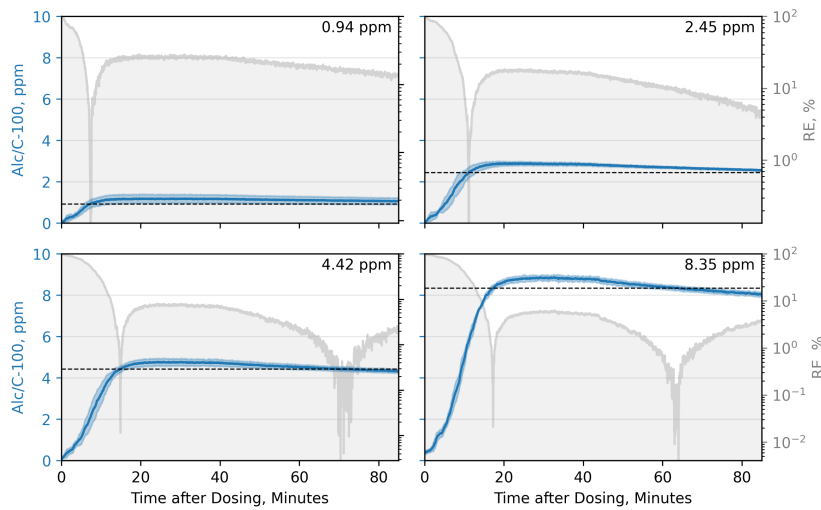


Figure 4.12: Mean concentration and standard deviation against the time after ethanol dosing was stopped. On the secondary y-axis, the absolute of the corresponding relative error is displayed. The mean predicted concentration by the software of the ASTRA is displayed in the upper right per panel and as a horizontal dashed line.

The shape of the concentration curve is similar for all samples: the initial increase in concentration starts at approximately zero) unlike gas dosing, where some of the gas

can already mix during the process). The increase to the maximum is first shallow, before continuing steeper. In all of the concentrations dosed, the maximum was reached before the 40 minutes of heating time elapsed. All dosed concentrations first exceeded the concentration predicted, before decreasing below. Like for carbon monoxide, the errors of the low concentrations (0.94 and 2.45 ppm) did not reach the second minima and decreased toward the end of the window, while for the two higher concentrations they increased.

The top panel in Figure 4.13 shows the identical data. The concentration maxima, marked with a black dot, are all reached, before the sampling. The lowest concentration evaporated earlier, due to the lower volume of liquid. As a consequence, the analysis curve in the bottom panel of Figure 4.13 shows, that more time is required for increasing dosed concentration to reach the maximum (using the same stock solution). The time until a peak maximum is reached was calculated using a linear fit, with C as the set concentration.

The trend of increasing duration with increasing concentration in Figure 4.13 is unlike Figure 4.11, where the required duration decreased with increasing concentration. In contrast to dosing a gas, the duration required to dose different concentrations of liquid differs only by seconds.

The dosing methods therefore show distinct dynamics in the initial mixing of concentrations within the ambient air. The heated liquids presumably first evaporate the alcohol before the water, leading to an initially high concentration and thus a rapid attainment of the maximum concentration. Additionally, set concentrations of the dosed liquid are approximately 0.4 ppm lower, due to an overshoot in mass. The actually dosed masses, corresponding to the set concentrations of the liquids, are listed in Table 4.5.

Table 4.5: Set concentration compared to set and actual mass dosed during liquid dosing. Approximately 0.04 g of stock solution was dosed on top of the desired amount on average.

Set Concentration, ppm	0.5	2.0	4.0	8.0
Set Masses, g	0.06	0.23	0.45	0.89
Mean of Actual Masses, g	0.10	0.27	0.49	0.93

4.2 Concentration Dependence on Time

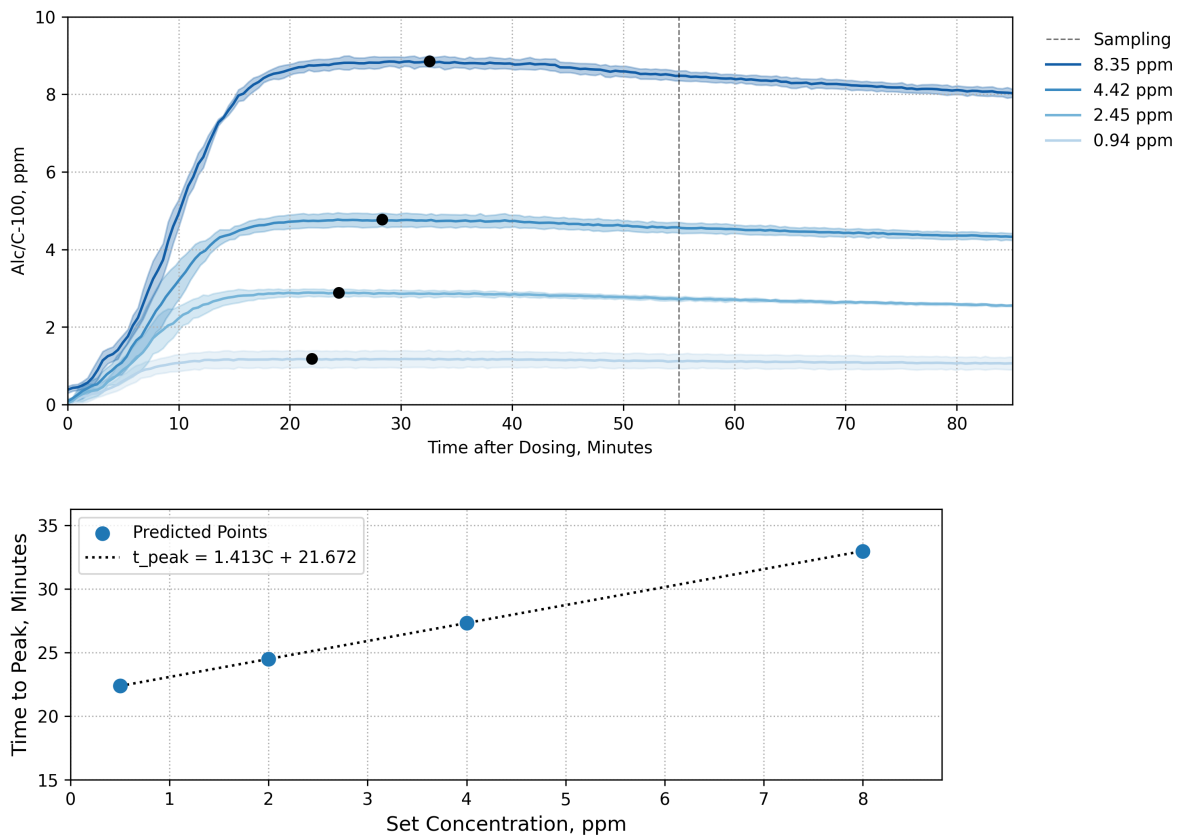


Figure 4.13: Dependence of EtOH concentration on time. Top panel: mean concentration and standard deviation, grouped and labeled by set concentration of repeated measurements against time, after dosing was completed. Black dots mark the maximum concentrations for the first time reached. Bottom panel: analysis function derived from the upper panel, describing the time required after dosing to reach the maximum.

Natural Decay

When the gas is left in the system, it will slowly decrease in concentration, due to the imperfect sealing of the glass chamber and its electronics. Such a process is displayed in Figure 4.14 for 15.03 ppm CO exemplary, with the start of dosing set to zero. A plateau is observable, where the concentration fluctuates between 14.5 and 15 ppm, before a steady decrease to 0 ppm, after approximately 22 hours. Even though this issue is still visible, it was improved largely in the development phase of the system.

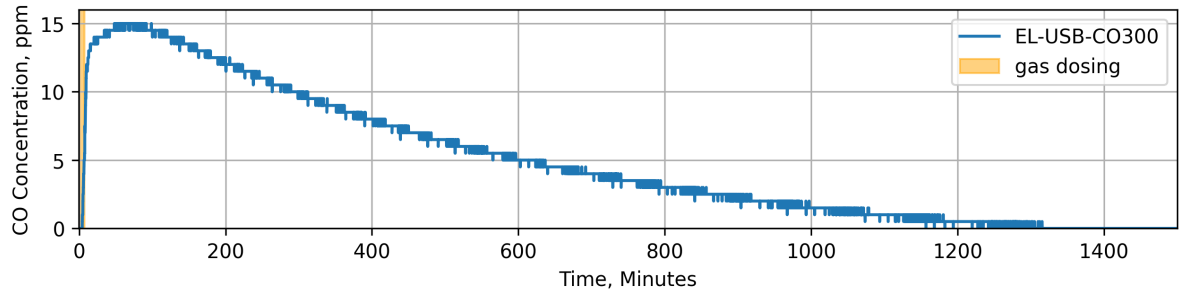


Figure 4.14: Carbon monoxide concentration over time, measured using the EL-USB-CO300, from the start of gas dosing until the decay to zero, without purging the air.

The time required for the concentration to be uniformly mixed in the system is much faster than the decrease of concentration through small holes in the construction. In the following, the concentration is therefore approximated to be constant and spatially uniform, with gradual loss of gas. Based on empirical measurements, the concentration decrease can be well described by a first-order exponential decay, leading to Equation 4.3 and 4.4. The rate of concentration decay was modeled using $C(t)$ as the concentration at time t , k as the rate constant and C_0 as the concentration at time zero.

$$\frac{dC(t)}{dt} = -kC(t) \quad (4.3)$$

$$C(t) = C_0 e^{-kt} \quad (4.4)$$

For visualization and calculation of the rate constant k , the last measured instance at the time of maximum concentration of three individual carbon monoxide measurements (5, 15 and 30 ppm) was set to zero. Low concentrations were intentionally chosen to not pollute the area with carbon monoxide. Yet, because of the low resolution of the

EL-USB-CO300, the natural decay at set 5 ppm could not be fitted and was therefore omitted. The concentration decrease is displayed against the time in Figure 4.15.

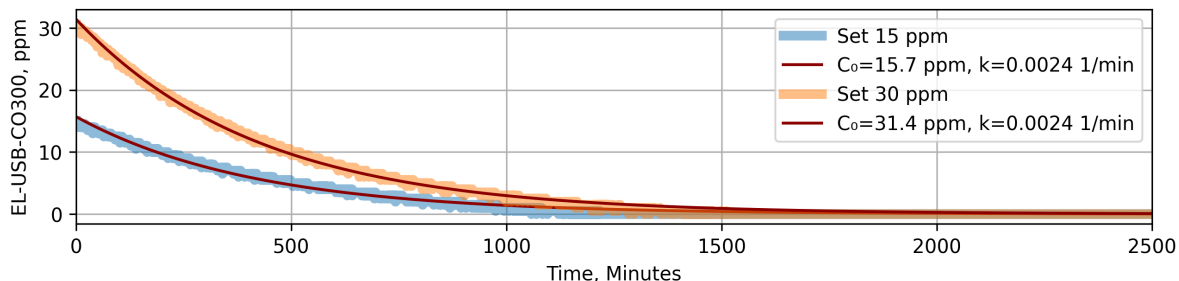


Figure 4.15: CO concentration decay as a function time without purging the air, measured using the EL-USB-CO300.

The rate constant k is 0.0024 min^{-1} for set 15 and set 30 ppm, indicating the decay follows first order kinetics. Even though the rate constant could differ depending on the set concentration and is influenced by the sensor dynamics, it is consistent with the assumption of a well-mixed volume governed by diffusive transport through the small holes. The configuration of the system was considered sufficient for hosting the experiments described in the works, as the diffusion out of the system is slow compared to the diffusion and mixing of gas within. Nevertheless, if necessary, the system can be further tightened to prevent leakage of analytes.

Forced Decay

Like for all the processes (except dosing), the duration of ventilation can be adjusted. To identify the minimum duration to completely clean the system, the concentration decay by forced ventilation (purge) was investigated. On account of the high speed of the process (and for this purpose insufficient resolution of the EL-USB-CO300, as visible for low concentrations in Figure 4.15) the electrochemical gas sensor of type Alc/C-100 was chosen for this measurement. Even so, the statements on minimum required ventilation time holds true for all measurements and sensors, according to the experimental data obtained. The time required to recover the sensors back to baseline is concentration dependent, nevertheless, after 30 minutes, the concentration reported by the sensor is at zero ppm.

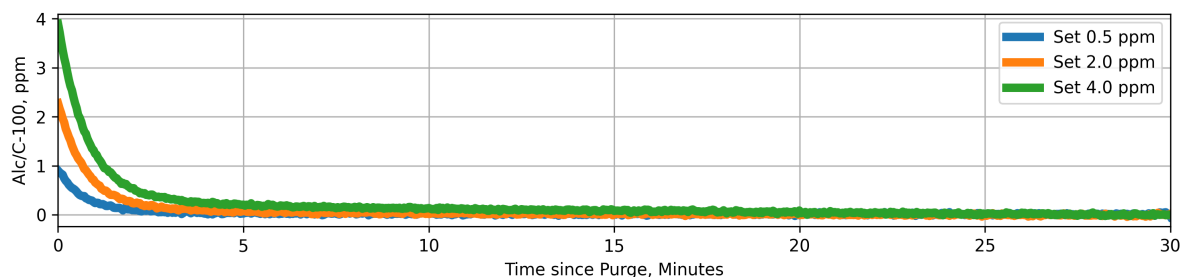


Figure 4.16: EtOH concentration decay as a function time while purging the air, measured using the Alc/C-100.

Based on the very steep slope in the beginning of the decay displayed in Figure 4.16, the concentration is highly time sensitive. Theoretically one could use this information to not only increase the concentration of analytes by the different dosing modes, but decrease it by controlled ventilation. In reality, the short half-life cannot be reached with sufficient accuracy, because of the delay in the electronics (for instance the time required for the shutters to close). Additionally, one would need to know the current concentrations C_0 (by reference electronics). This is expected to be increasingly difficult for mixtures in the system, with sensor readings limited by response times and cross-sensitivities. Additionally, one has to account for the recovery time of each sensor, which is often not explicitly stated by the manufacturers.

Minimum Ventilation Time

For CO concentrations up to 60 ppm, 30 minutes of ventilation led to the sensor recovering back to the baseline in the subsequent 30 minutes equilibration time (without injecting analyte). This late recovery suggests, that the system is cleaned within 30 minutes of ventilation, yet sensor recovery is the rate-determining step. In conclusion, 30 minutes of ventilation are sufficient if there are 30 minutes added for the sensor to recover, resulting in a total of 60 minutes. For ethanol similar behavior was observed.

Minimum Heating Duration

The duration for heating is advised to be set to 40 minutes, because this, with the current power supply connected and the voltage set to 11 V, is sufficient to evaporate a maximum mass of up to 1.0 g per basin. This maximum mass is variable and can be changed in the configuration of the input file, used by the software QBPY to give an error when exceeded.

Gas Mixtures

To make predictions about the concentrations of analytes in gas mixtures, the concentration in the system and its decay should be calculated per analyte individually or even better measured on-line. The reason is, that the gases are being dosed at the same time: when the set concentration of one gas is reached (according to the calculations of QBPY), the dosing is stopped, while the other gases are continuously dosed until they reach their set concentration. Liquids are added after the gas dosing, if not specified differently in the input file. Therefore, the perfect alignment of concentration maxima using several different analytes poses difficulties. Nevertheless, a short measurement series was conducted to identify possible interferences of two gases being dosed simultaneously with the EL-USB-CO300, which is not cross-sensitive to EtOH in the concentrations reported.

Since ethanol was dosed as gas coming from a pressurized bottle, a measurement series was conducted to ensure that the dosing is approximately accurate. The resulting errors after 15 minutes of the assessment, conducted in the same way as previously reported for carbon monoxide, is supplied in Table 4.6, and the evolution of gas over time in the *Appendix*, Figure 9.2.

Similar as for CO, the actual values are higher than the predicted concentrations for all,

except one data point at 0.51 ppm, indicating that the gas dosing mechanism leads to a slightly higher concentration than estimated. The process is expected to be gas type, time and concentration dependent. However, the time series are similar to those of CO, suggesting the process is dominated by the dosing mechanism rather than gas dependent effects, such as molecular speed or interactions.

Table 4.6: Mean errors for calculated concentrations of EtOH, supplied by the gas dosing mechanism of the ASTRA and actual concentrations obtained using the Alc/C-100.

Mean Predicted Concentration, ppm	MRE, %	MAE, ppm
0.51	8.96 ± 10.95	0.06 ± 0.07
2.01	21.76 ± 2.24	0.56 ± 0.07
4.01	23.26 ± 0.98	1.22 ± 0.07
8.01	21.98 ± 2.09	2.26 ± 0.28

Sequentially, 15 ppm CO was dosed three times, then again with different concentrations of EtOH (1 ppm, 2.5 ppm, 5 ppm). This measurement was repeated with a blank being synthetic air, instead of EtOH. As a comparison, the whole series of measurements was repeated for 30 ppm carbon monoxide.

The sampling time was again set to 15 minutes after finished gas dosing. Thus, in the case of ethanol dosing requiring more time, carbon monoxide has already started to distribute within the system. These differences are approximately 10 minutes for 15 ppm CO with 5 ppm EtOH, 1 minute for 15 ppm CO with 2.5 ppm EtOH, and 1 minute for 30 ppm CO with 5 ppm EtOH. Depending on the case, the exact stop of dosing per analyte should be considered and can be found in the data, logged by QBPY.

Table 4.7 shows the mean errors. The full table containing the single samples can be found in the *Appendix* in Table 9.1. The errors of pure CO are the lowest, but have the largest deviation, while the ones obtained during simultaneous EtOH dosing are the highest error with lowest deviation. The errors for approx. 30 ppm are very similar in value. When comparing the errors and standard deviations, no significant deviations can be observed.

Table 4.7: Relative errors for calculated concentrations by the ASTRA and actual concentrations obtained using the EL-USB-CO300 during gas mixtures.

Calculated Concentration, ppm	Added Gas	MRE, %	MAE, ppm
15.04	-	7.93 ± 3.21	1.24 ± 0.51
15.06	syn. air	9.62 ± 1.48	1.61 ± 0.28
15.04	EtOH	11.53 ± 0.11	1.96 ± 0.02
30.05	-	7.28 ± 1.42	2.36 ± 0.50
30.05	syn. air	6.09 ± 0.01	1.95 ± 0.00
30.06	EtOH	6.81 ± 0.81	2.20 ± 0.28

With this chapter, a brief performance assessment of the ASTRA was reported with suggested ventilation and heating durations, as well as examples of test gas calibrations. A time dependent approximate on the actual concentration of CO and ethanol was provided, in addition to the deviation from the concentrations reported by the custom software QBPY. Given the highly modular structure, which can be adapted to individual experimental requirements, the metrics and equations that were described should be regarded as guidelines, rather than binding specifications. If information of the exact concentration of analytes is required, the system can be equipped with additional reference electronics.

The ASTRA provides an ideal test facility for robust training in ambient air conditions. As intended, this system can be used to introduce additional gases, train sensors, and evaluate their performance in short or long-term experiments. The system delivers a semi-controlled environment, compared to the highly controlled standard GMS or the complex real-world applications.

5 Temperature Predictions

This chapter covers the studies on the SGP40, measuring the thermally induced outgassing from the selected materials, to predict the temperature first qualitatively, then quantitatively. Starting with an exploratory study, performing threshold-based classification on the basis of PMMA, the measurement campaign was extended to more granular temperature-increments, using all four materials. Both studies were published and presented at the *53th and 54th International Conference on Environmental Systems* [148, 149], as well as partly at the *17. Dresdner Sensor-Symposium* [150], while the contents of the second, longer study in 5.2 extend beyond the published work.

Identifying the Temperature Range

The first step towards the goal of developing a pre-ignition fire detection system, is to gain knowledge about the properties of the selected modified polymers. Information about the behavior of the materials under thermal stress (regarding their degradation temperature), and with this, identification of the temperature range at which the sensors should be able to safely detect additives, is necessary.

Using TGA-MS as described in Section 3.4, the temperatures at which 90 % and 95 % of the mass remains, were identified and listed in Table 5.1. These limits should not be exceeded to prevent the degradation of the material and detection of polymer backbone degradation products, instead of additives released pre-ignition. The temperature at which 95 % of the sample mass is still intact, is considered too high. Between 95 % and 90 % of remaining mass, only 8 K difference were measured for PMMA, revealing a fast progress in degradation. The further degradation of Nomex from 95 % to 90 % took 20 K, while PDMS and Kapton showed the same percentage of mass loss after additional 12 K. For the safety of the equipment, the selected maximum temperatures for the overheating measurements were set roughly 100 °C lower (see Table 5.2).

The exact temperature considered safe is largely dependent on the application and has to be decided on specifically for each case. Simone et al. [151] demonstrated the

Table 5.1: Temperatures at which 95 % and 90 % of the initial mass remain. Extracted from [148].

Remaining Mass	PMMA	PDMS	Nomex	Kapton
95 %	280 °C	389 °C	407 °C	560 °C
90 %	288 °C	401 °C	427 °C	572 °C

Table 5.2: Maximum furnace temperatures during overheating tests in the ASTRA. Based on [148].

PMMA	PDMS	Nomex	Kapton
200 °C	250 °C	300 °C	450 °C

importance of elaborated tests of changed flammability, depending on the material configuration. For example, the damage by the flame after ignition of polyvinylidene fluoride bags greatly increased when being filled with polyester wipes. In a similar manner, even without ignition, the configuration of the modified polymer, including ambient conditions like oxygen content and pressure, has to be taken into consideration when selecting a threshold (TH) temperature for detection.

Using a mass spectrometer, coupled to the thermogravimetric analyzer, an attempt to find the outgassing species was made, with the aim to link them directly to certain temperatures. Onsets and steps in the sensor response (sudden increases in sensor signal linked to increases in temperature) could then be explained by additives or monomers exiting the investigated materials. With these species known, the sensors could potentially be trained to detect selectively and distinguish from interfering gases. Although mass-to-charge ratios were obtained, the assignment to meaningful molecules turned out to be challenging, especially at low material temperature, where the detection should ideally take place. Some findings are published in [148], nevertheless, the empirical process of repeated measurements of the heated materials was chosen and conducted as reported in the following chapters. To conclude, limits of safe temperature THs for detection in the following experiments were set (in terms of stability of the material), yet the second part of the objective to identify the species found as (early) outgassing was only met to a certain extend using TGA-MS.

5.1 Binary Detection on PMMA

As reported in [148] and [150], an exploratory study, testing the tube furnace and the SGP40 for their suitability, was conducted on PMMA. A calibration of the tube furnace revealed that the deviation from set to actual temperature ranges from 1.15 % to 2.84 % with a maximum deviation of ± 3 K.

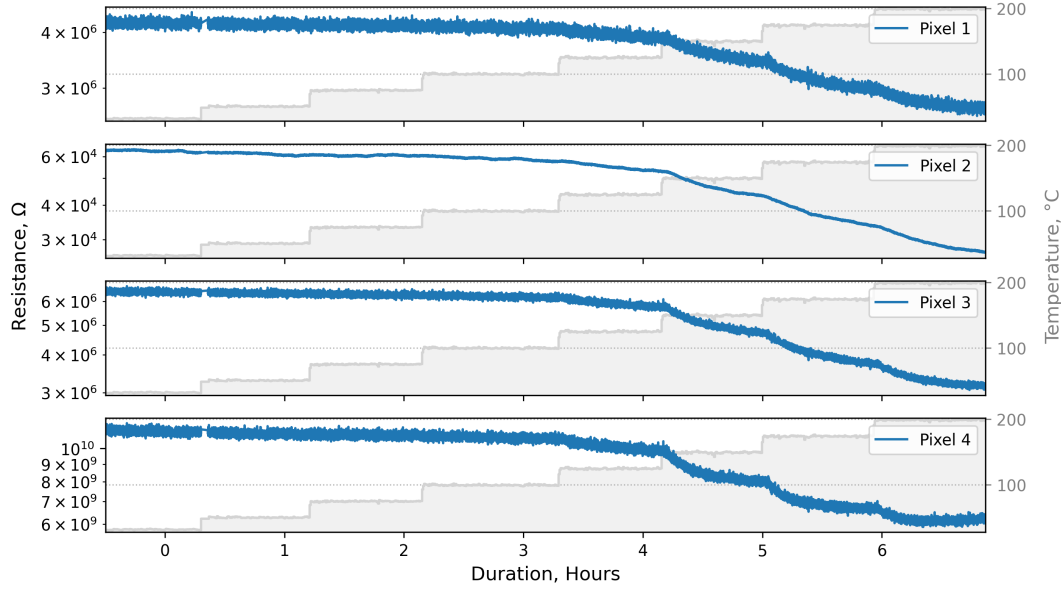


Figure 5.1: Resistance of the four sensing materials against time. On the second y-axis, the actual furnace temperature is plotted, visualized in the panels in grey. Adapted from [148].

Inside the ASTRA, the furnace was placed close to the slow-rotating fan. A PMMA sample of 200 mg was placed onto a quartz glass boat and pushed into the middle of the furnace, using a marked rod. The day after sample preparation, the measurement was conducted and afterwards the system was ventilated completely. The SGP40, operated at 300 °C, measured the outgassing with a sampling frequency of 1 Hz, approximately 1 m distant from the furnace. As visualized in Figure 5.1, the temperature was increased every 50 minutes with the pixels starting to show a significant reaction at around 100 °C. All of the four pixels clearly react to the outgassing with a noticeable decrease in resistance for increase in temperature, and with significant differences in magnitude, influencing the perceived noise.

The measurement was repeated four times, each time with a fresh sample from the same batch. An additional run was conducted in an identical manner, but without any sample

inside the quartz glass boat to identify possible outgassing by the device itself. To obtain a comparable, baseline-independent metric, the sensor signal was calculated as the ratio of the mean of the last 180 data points at the lowest temperature (here 25 °C) to the mean of the last 180 data points at the respective temperature.

The sensor signals of the repeated samples in comparison to the sensor signals of the glass boat clearly prove, that the outgassing of the tube furnace and boat is negligible in comparison to the outgassing of PMMA, released at temperatures above 100 °C. While the sensor signals of all four pixels followed the same trend, pixel 2 reacted with the highest values. The signal of pixel 4 progressed with the least steep increase toward the last temperature step, seemingly approaching saturation.

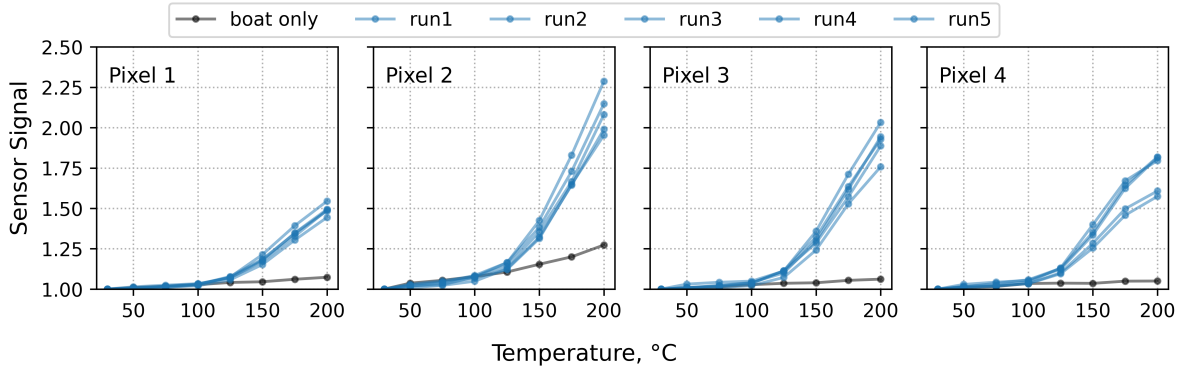


Figure 5.2: Sensor signals of all five measured PMMA samples and a blank against the furnace temperature. Adapted from [148].

Using the five PMMA measurements, a LDA was conducted based on the logarithm of the last 540 data points per temperature step, grouped into packages of three minutes, and flattened to a vector of length 180×4 (pixels) = 720* per package. The data, containing the responses of all four pixels, was split into 80 % training data and 20 % for testing. This corresponds to four days/runs as training and the remaining, unseen run for testing. Because no hyperparameter tuning was conducted, using `scikit learn`'s `LinearDiscriminantAnalysis` with its default parameters, the sectioning of a validation set was omitted.

* Multiples of 180 data points (equivalent to 180 seconds) are used because this interval exactly matches the duration of a complete temperature modulation cycle. As reported in [148], a comparison of the sensor operated at constant 300 °C, with two different temperature modulated sensors, led to the conclusion that the constant-temperature sensor performed better. This effect is likely due to the limited dataset size, which is insufficient to robustly learn the more complex and diverse feature space introduced by temperature modulation.

In total, five independent models were trained, each time splitting the data in a way, that a different run was left out for testing. To quantify the ability of the sensor to correctly identify the temperature exceeding a certain level, the metrics recall and precision were employed, using:

- true negative (TN), correctly identified as below the selected TH
- false positive (FP), wrongfully predicted as above TH or type 1 error
- false negative (FN), wrongfully prediction below TH or type 2 error
- true positive (TP), correctly identified above the selected TH

By using Equation 5.1 and 5.2, recall and precision were calculated for each temperature, except the baseline. The mean values of recall and precision per temperature TH, obtained from the five normalized confusion matrices, are listed in Table 5.3.

Recall and precision are above 0.8 for all THs. The prediction for temperatures above 150 °C is immaculate and none of the five matrices shows mispredictions. Below perfect detection, the highest recall was achieved at 125 °C and the highest precision equally at 50 °C and 125 °C.

$$\text{Recall} = \frac{TP}{TP + FN} \quad (5.1)$$

$$\text{Precision} = \frac{TP}{TP + FP} \quad (5.2)$$

Table 5.3: Recall and precision values of different TH temperatures obtained from the mean recall and precision values of all five confusion matrices. The THs are obtained from the set furnace temperature for the purpose of grouping in the classification. Reprinted from [150].

TH	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C
Recall	0.93	0.96	0.95	0.97	1.00	1.00	1.00
Precision	0.93	0.92	0.88	0.93	1.00	1.00	1.00

Continuous Heating

An additional experiment was conducted to evaluate, whether a model, trained on sensor responses to the outgassing of gradually heated PMMA, can accurately predict the temperature of continuously heated material (which more closely reflects real-world application conditions). Figure 5.3 shows the resistance of the pixels over time, based on the increasing temperature of the furnace. The decrease in resistance is visual, starting at around 125 °C, for all four pixels. A steady response of pixel 4 can be observed toward the end, while the other sensing elements show decreasing resistance.

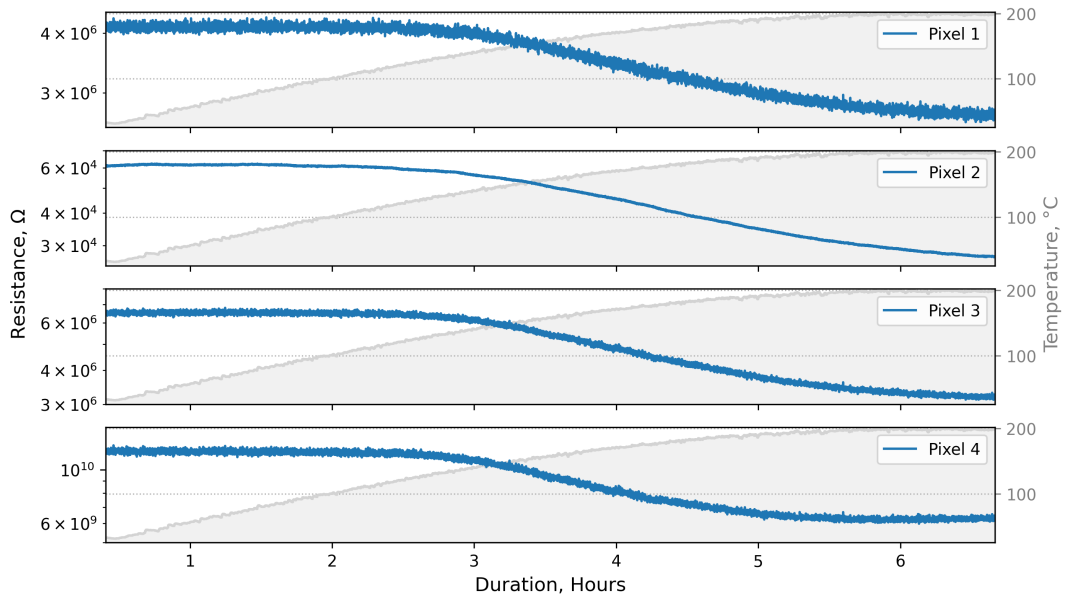


Figure 5.3: Resistance of the four sensing elements against time, during continuous heating of the PMMA sample. On the second y-axis, the actual furnace temperature is plotted, visualized in the panels in grey. Adapted from [148].

The training data for the LDA consisted of the last 180 data points per temperature from all the five runs, measuring the PMMA outgassing by the stepwise increased furnace temperature. The test data contained 180-point packages labeled with zero or one, depending on whether the last (set) temperature of the respective package is above or below the respective TH. When comparing the results of the different THs in Table 5.4, it has to be taken into consideration that statistically, the number of events below or above the TH used for the calculation of recall and precision varies. For example, with low THs, there are only a few values that are lower (marked as zero), while high THs will have fewer values above. By this logic, the lower THs lead to high precision values,

which should decrease with increasing TH value, as visible for 175 °C and 200 °C. When disregarding this last statistically disadvantaged temperature TH, the precision values are all above 0.8. Values for recall drop in the middle of the temperature range, possibly because of the fast changes during continuous heating, compared to the stepwise increase, leading to great differences in amount and kind of outgassing species. This observation is based on a fundamental limitation of machine learning models: accurate predictions are generally restricted to interpolation within the range and conditions covered by the training data, while extrapolation remains unreliable. Despite this limitation, the sensor shows a strong performance, especially at 175 °C.

Table 5.4: Recall and precision values of different TH temperatures obtained from the continuous PMMA measurement as test set. Reprinted from [148].

TH	50 °C	75 °C	100 °C	125 °C	150 °C	175 °C	200 °C
Recall	0.95	0.81	0.74	0.71	0.88	0.96	1.00
Precision	0.95	0.86	0.92	1.00	1.00	0.96	0.58

After successful binary detection using the SGP40, the applicability of the concept and suitability of the sensor for the given material is proven. The tube furnace showed to be of great value, especially, because of the constant temperature feedback and automatic adjustment of temperature.

5.2 Predicting Material Temperature from Outgassing

The content of this chapter is partly based on a previous publication and the respective dataset [149], however, the following evaluation provides a more comprehensive analysis. Moving to semi-continuous heating allows for the prediction of continuous temperatures from the simulated overheating of the selected materials. The amount of data and the high resolution in temperature, enables the use of regression models. To quantify the performance, different errors such as root mean squared error (RMSE), MAE, MRE, and the coefficient of determination (R^2) were consulted.

The measurements were conducted by selecting a minimum of 50 °C and the material dependent maximum temperature. In this range, per experiment, 26 random steps were chosen, in a 5 °C equidistant grid, to be held for 15 minutes by the tube furnace. The temperatures reported are the set temperatures, if not stated explicitly. The semi-random step increase was chosen as an alternative to a natural, continuous temperature rise. By heating in this fashion, a variation in distinct temperatures was introduced, to prevent the model from relying on known history or sequences. Given that the process of material overheating, as it would occur in an actual application, is unpredictable (due to the complex and changing environment) and therefore cannot be precisely reproduced during training, the training data should incorporate some variation. Introducing irregularity by choosing random steps into the temperature sequence ensures more generalized learning, by providing a more robust dataset.

A total of 46 measurements were recorded: 15 Nomex, 9 PMMA, 11 Kapton, and 11 PDMS samples. A fresh sample from the same batch was used for each run. SGP40 sensors were placed 1 m distant from the tube furnace, out of which one was operated at a constant temperature of 300 °C, while six others were operated in temperature modulation (as displayed in Section 3.1, Figure 3.1). This data was acquired with Haile Solomon in the course of his admission paper [130].

Univariate Analysis

From the sensors utilized, one sensor operated at constant 300 °C was evaluated in regard to the sensor signals of the four pixels.

Figure 5.4 shows the mean and standard deviation of the sensor signals for all of the samples, per material. Pixel 1 started to show a reaction to PMMA at roughly 125 °C, and to Nomex at approximately 155 °C. The onset suggest that gases exit the material after that TH is reached. Based on the calibration, the actual furnace temperature deviated by a maximum of ± 3 K from the set temperature, so even with a delay in the response of the sensors, the actual TH of additives exiting the polymer matrix should be close to the temperature measured.

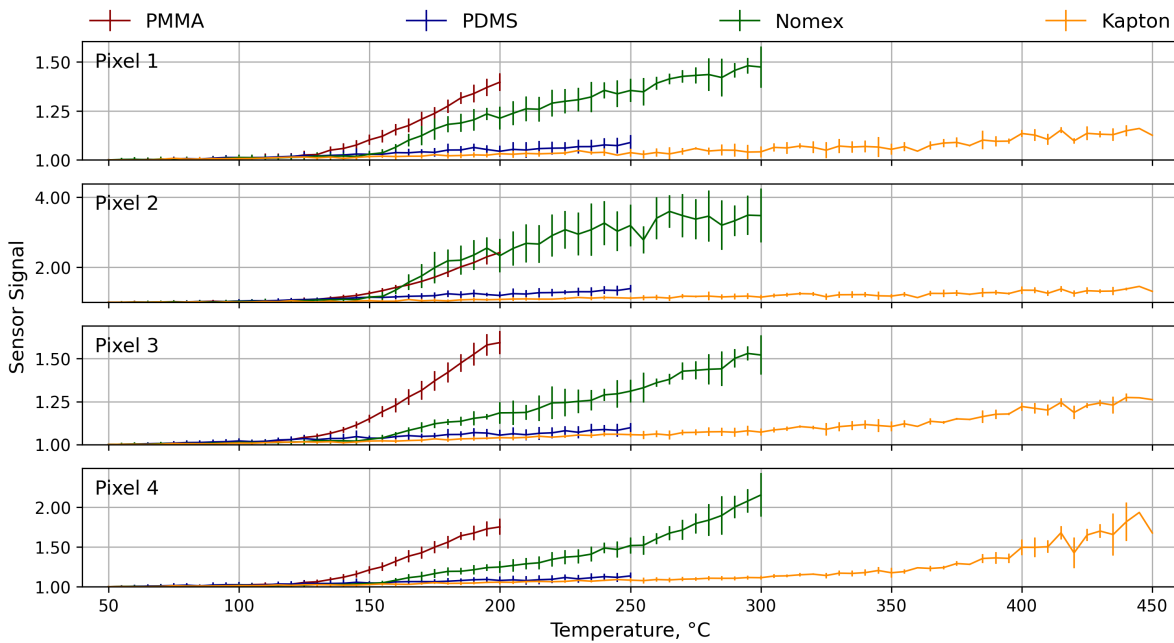


Figure 5.4: Mean and standard deviation of the sensor signals per pixel, for all materials. Adapted from [149].

Only a shallow increase in sensor signal can be observed from the measurements obtained with pixel 1. The measurements of Nomex resulted in the highest sensor signals and the highest variation measured with this pixel. The data of pixel 2 reveals a similar trend of onsets for PMMA and Nomex, while measuring insignificant changes during the heating of PDMS and Kapton. The sensor signals of pixel 2 towards Nomex exceed the signals of PMMA from approximately 165 °C on, yet with high deviation measured in between the samples. Pixel 3 reacts strongest to PMMA, followed by Nomex. Pixel 4 exhibits

the largest response to Nomex, at its highest temperature. Out of all the pixels, the highest sensor signals to Kapton can be observed with pixel 4.

As expected and necessary, the pixels show different responses to the materials' outgassing, due to the presumably different materials of the sensing units, forming the array on the SGP40.

The reaction of the sensor to PDMS could not be reproducibly distinguished from a blank sample (furnace temperature program with an empty glass boat as sample). In the upcoming analysis, the discussion on PDMS is still carried out, but could be regarded as similar to a blank sample, nevertheless, the complete absence of any measurable species cannot be assumed.

To conclude, the reliable detection of outgassing by the SGP40 was proven for all materials, except PDMS. When aiming to measure Kapton, pixel 4 should be selected, at material temperatures above 350 °C, while PMMA and Nomex can be reliably measured starting at 125 °C and 155 °C onward using any of the pixels.

Multivariate Analysis

For the multivariate analysis of the data, all four pixels were evaluated to identify the temperature of the material using different machine learning techniques, namely: ridge regression, random forest regression and XGBoost regression. These algorithms differ in their bias-variance trade-off and data requirements. Additionally, ridge regression assumes a linear relationship in the data (for more information see Section 2.3).

The raw resistance data was pre-processed per sensor (in constant, or in temperature modulation mode), by arranging the data in 180-point packages to match the length of a full temperature modulation. Concerning modulated sensors, the temperature modulation was kept intact using the variable *ramp_id**, unique per temperature cycle. To process the recordings of the sensor operated at constant 300 °C, the data-packages were assigned to increasing integers to compare to *ramp_id*. The logarithm of the data was taken and arrays were formed containing all the information of a full 180-points-package of all four pixels, with the label being the last temperature the furnace was set to, per package. Because of occasional time outs of the ESP32 and the selection of full modulations only, the net amount of data points is less for the modulated sensors, compared to the sensor operated at constant temperature. This

* For more information on the structure of the obtained data and the operation of the (temperature modulated) sensors see [131]

disadvantage could be artificially reduced by dropping the same amount of data from the sensor in constant operation, but as this is a realistic issue with the use of modulated sensors and live data transmission, it was kept as is.

The data was split into 30 % test set, 56 % training, and 14 % of data for validation, using the same `random_state` each time, to ensure reproducibility. The training data was used to train models for all possible hyperparameter combinations in a grid search (because of their possible correlations) and validated on the validation set. The best performing mode was kept, and the resulting model tested on the unseen data. The choice of error metrics for model selection was based on the advantage of the RMSE penalizing larger errors. Small deviations in temperature are acceptable but larger deviations should be avoided. As a result, the RMSE is very sensitive to outliers. The chosen parameters per model are listed in the *Appendix*.

First, the results using the sensor operated at constant temperature are discussed, before comparing the results obtained with the best performing of the sensors operated in temperature modulation (TMM 2). The results obtained with the remaining five sensors in different temperature modulation modes are included at the end of the chapter, for completeness.

Sensor at 300 °C – Single-Material Analysis

In the bar plots in Figure 5.5, the split of the data obtained with the sensor operated at constant 300 °C is visualized. For each material, the training data is visualized in blue, the validation data in orange, and test data in green. With this split, the machine learning models were trained, validated, and tested. In the following, the results obtained with the test set are discussed.

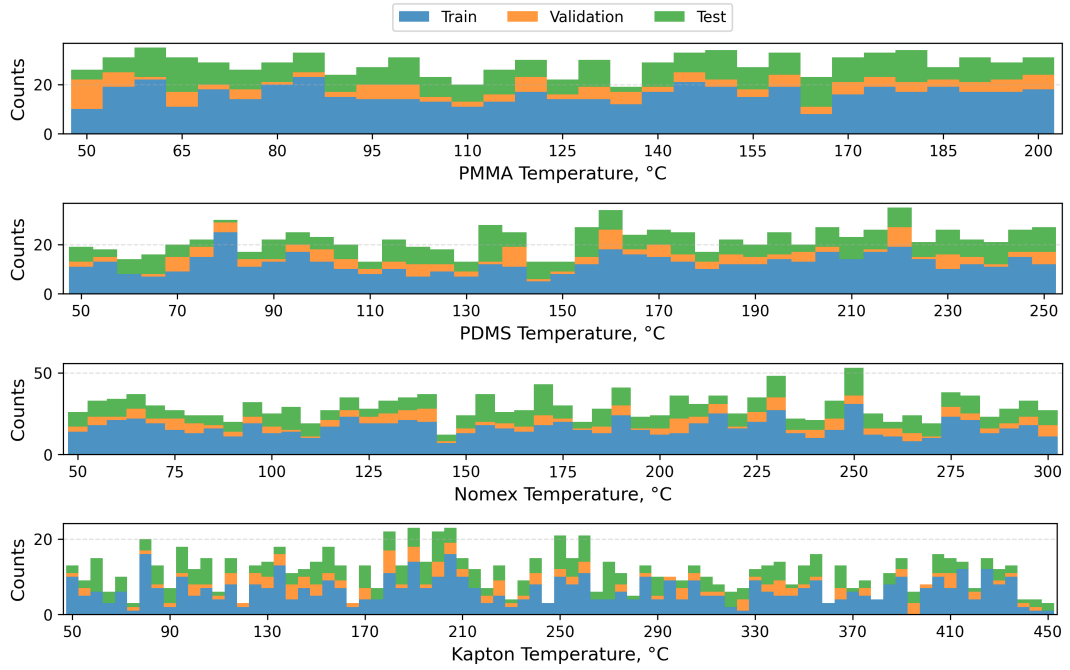


Figure 5.5: The count of each of the temperatures is stacked for training, test, and validation data, obtained with the sensor operated at constant temperature. The top figure shows the distribution of the train-validation-test split for PMMA, below PDMS, then Nomex, followed by Kapton.

The results of the ridge regression are displayed in the first row of Figure 5.6. The onset, identified earlier for PMMA and Nomex (in Figure 5.4), is visible in the respective parity plots. The temperature of PMMA is predicted as 100 °C, until the actual temperature of approximately 125 °C is reached, which is in correspondence with the findings of the univariate analysis. The onset temperature of Nomex becomes visible shortly after 150 °C, again in agreement with the previous results.

The predicted data by the random forest regression (Figure 5.6, second row), shows a more linear behavior for PMMA and Nomex, but slightly larger spread for Kapton around 250 °C. The data in the parity plot from PDMS seems to show a S-shaped

5.2 Predicting Material Temperature from Outgassing

curvature. For all materials, the predicted data meets the actual data better, compared to the predictions from ridge, especially at the higher end of the respective temperature range, where the data shows low spread from the diagonal.

XGBoost delivers no significant improvements visually, but less spread for Kapton in the middle of its temperature range and at the lower end for PMMA.

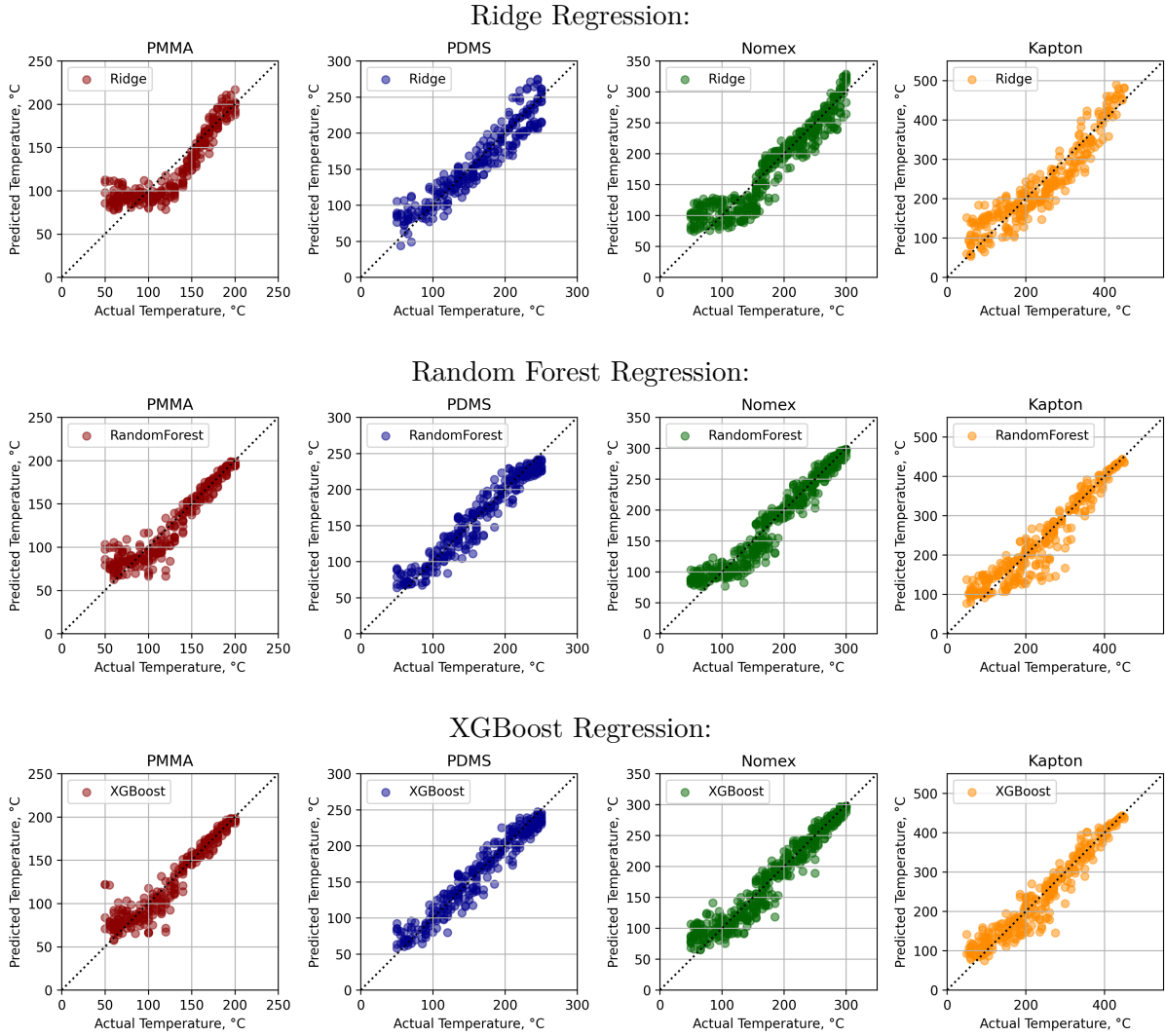


Figure 5.6: Parity plots showing predictions by ridge, random forest, and XGBoost regression against actual temperatures. All data originates from the previously unseen test set of the respective material, recorded by the sensor operated at constant 300 °C. In part adapted from [149].

The errors listed in Table 5.5 show large improvement in RMSEs and MAEs for all materials from ridge regression to random forest, less significant to XGBoost (unobservable for Nomex). R^2 shows improvements for materials and algorithms from top to bottom, except Nomex from random forest to XGBoost. The MRE follows similar trends, but without further improvement from random forest to XGBoost for PDMS. In conclusion, the material temperatures can be identified with low errors, and the overall best performances were obtained using XGBoost.

Table 5.5: Model performance metrics of the single-material test set, recorded by the sensor operated at constant 300 °C.

Material	Regression Model	RMSE, K	MAE, K	MRE, %	R^2
PMMA	Ridge	19.94	16.05	17.31	0.80
PMMA	RandomForest	14.67	10.27	11.58	0.89
PMMA	XGBoost	14.38	9.48	10.74	0.90
PDMS	Ridge	18.74	14.76	11.76	0.90
PDMS	RandomForest	15.01	11.96	9.42	0.93
PDMS	XGBoost	14.48	11.38	8.83	0.94
Nomex	Ridge	23.81	18.67	16.24	0.89
Nomex	RandomForest	18.36	14.07	12.43	0.94
Nomex	XGBoost	18.38	13.89	12.26	0.94
Kapton	Ridge	38.28	31.98	20.21	0.88
Kapton	RandomForest	34.71	25.53	17.45	0.90
Kapton	XGBoost	30.46	23.19	15.53	0.92

Sensor at 300 °C – Multi-Material Analysis

In reality, all the materials might be present simultaneously, while one is undergoing a rise in temperature. To simulate such a situation and provide an answer to the question about the ability of the sensor to distinguish the materials based on their outgassing, all data is combined. While one material was heated, the temperature label of the other materials can be set to 25 °C (approximately room temperature) based on the results of the univariate analysis (Section 5.2), showing the earliest significant onset in sensor signal and therefore measurable outgassing at 125 °C. Small amounts of additives might have been released earlier on, but realistically not in significant amounts.

The data pre-processing was conducted in the same manner as for the single-material

5.2 Predicting Material Temperature from Outgassing

analysis and the models were trained, validated, and tested on the same ratio. The model selected as best performing (by global multi-output RMSE) was used for the final data prediction. The choice of training only one model for all materials, instead of four separate models, was based on the application, where one model should suffice. If necessary, the influences of the materials' RMSEs could be weighted in further tests. The parity plots in Figure 5.7 and Table 5.6 show the actual versus predicted data, for the respective material (extracted from the full matrix of data).

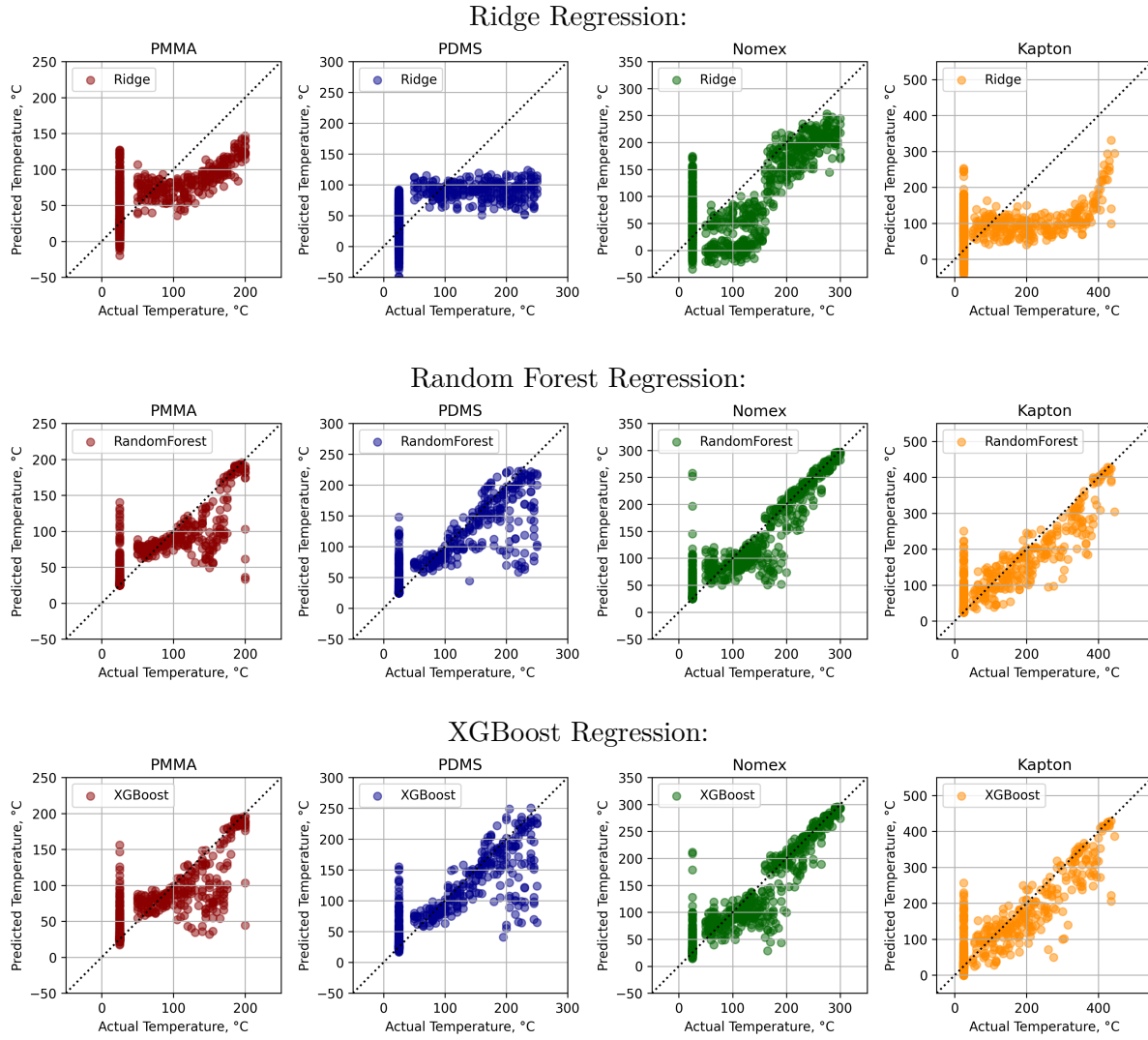


Figure 5.7: Parity plots showing predictions by ridge, random forest, and XGBoost regression against actual temperatures. All data originates from the previously unseen test set of the combined materials, recorded by the sensor operated at constant 300 °C. In part adapted from [149].

Regarding the ridge regression, the performances are overall significantly worse when the data is combined. A line at the 'actual' temperature of 25 °C is visible, making an accurate prediction at the spread of this line impossible. For instance, the output of the ridge regression, using the data of PMMA, shows that no temperature below approximately 130 °C can be correctly identified. In this region, the material could be either unheated or heated to 200 °C (e.g., predicted 125 °C = actual 25 °C OR actual 200 °C; predicted 60 °C = actual 25 °C OR 50–110 °C). For the other materials the issue is similar. PDMS visibly performs badly. A prediction below 50 °C corresponds to an actual temperature of 25 °C and anything above translates into any possible temperature in the range of 50 to 250 °C. The low R^2 of 0.3 in Table 5.6 reflects that. The prediction of Nomex is at least somewhat reliable above 180 °C. Despite large deviations from the diagonal, the behavior remains roughly linear. Kapton can only be identified as hot for predicted temperatures above 250 °C and even then, inaccurately, with an R^2 of 0.19. Improvement becomes visible when using tree-based regression, which does not assume linearity in the data, as ridge regression does. Nevertheless, more outliers are produced in the predictions. The predicted temperatures, above the vertical line at actual 25 °C, follow the diagonal, but are partly wide spread. The improvement from ridge to random forest is observable in the errors in Table 5.8 as well. Especially the MAE is less than half as big for the ridge regression and the R^2 is more than double for PDMS and Kapton. XGBoost regression shows outliers in the data, however, they seem less extreme compared to random forest. Overall, the results using random forest perform best or similar to XGBoost. Exceptions are the RMSE and R^2 of Nomex and the MRE of PDMS (see Table 5.6).

Table 5.6: Model performance metrics of the combined-material test set, recorded by the sensor operated at constant 300 °C.

Material	Regression Model	RMSE, K	MAE, K	MRE, %	R^2
PMMA	Ridge	35.07	26.24	76.08	0.39
PMMA	RandomForest	21.82	9.42	20.25	0.76
PMMA	XGBoost	22.37	9.81	20.89	0.75
PDMS	Ridge	50.26	37.42	96.25	0.30
PDMS	RandomForest	25.84	10.69	20.58	0.81
PDMS	XGBoost	26.10	10.58	20.66	0.81
Nomex	Ridge	55.11	43.95	103.77	0.57
Nomex	RandomForest	25.02	12.17	23.87	0.91
Nomex	XGBoost	23.94	12.32	23.79	0.92
Kapton	Ridge	86.60	64.11	162.60	0.19
Kapton	RandomForest	35.92	16.39	34.59	0.86
Kapton	XGBoost	37.81	17.85	39.91	0.85

In summary, the success in prediction and differentiation of the materials from the combined dataset is limited. The RMSE is (significantly) worse for models and materials moving from the single to the combined material analysis. The MAE on the other hand, shows a decrease in errors from single to combined analysis for all materials and models, except ridge regression, as well as for XGBoost on the PMMA data. The decrease in error presumably occurs due to most of the models yielding accurate predictions in the dataset, now largely dominated by samples labeled as 25 °C. If these predictions are of low error, the mean absolute error is low. In contrast, the MRE shows errors relative to the actual temperature and the RMSE is putting more weight on the large errors and outliers, which are significantly more for all models and materials in the combined dataset.

Sensor in Temperature Modulation – Single-Material Analysis

The results obtained with sensor operated in TMM2 are reported in the following. Details on the modulation shape can be found in Section 3.1 and background information on the fundamentals of the technique in Section 2.2. At first, the data is presented for each material, and in the subsequent section, the combined data is shown. The evaluation was done as previously discussed, in the same fashion as for the sensor operated at 300 °C. The split of the data per material is visualized in Figure 5.8, with the height of the three plots combining to the total number of counts per temperature, respectively.

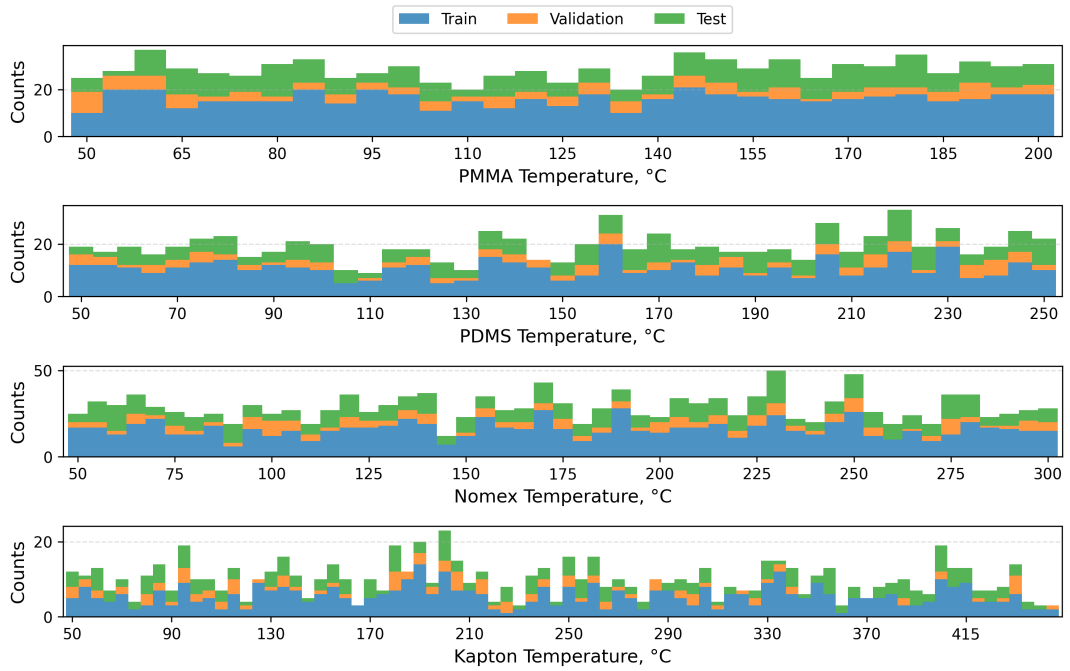


Figure 5.8: The count of each of the temperatures is stacked for training, test, and validation data, obtained with the sensor operated in temperature modulation. The top panel shows the distribution of the train-validation-test split for PMMA, below PDMS, then Nomex, followed by Kapton.

Looking at the parity plots obtained with ridge regression (Figure 5.9, first row), less pronounced kinks in the predictions for PMMA and Nomex, caused by the onset in sensor signal, are visible. The predictions on Kapton appear comparable to the results obtained with the sensor at constant temperature, here showing a slightly larger spread. The PDMS data shows a larger spread for all of the models. The improvements, by using random forest regression in comparison to ridge, are highest for PMMA and Nomex, with less significant further improvements by XGBoost (Table 5.7).

5.2 Predicting Material Temperature from Outgassing

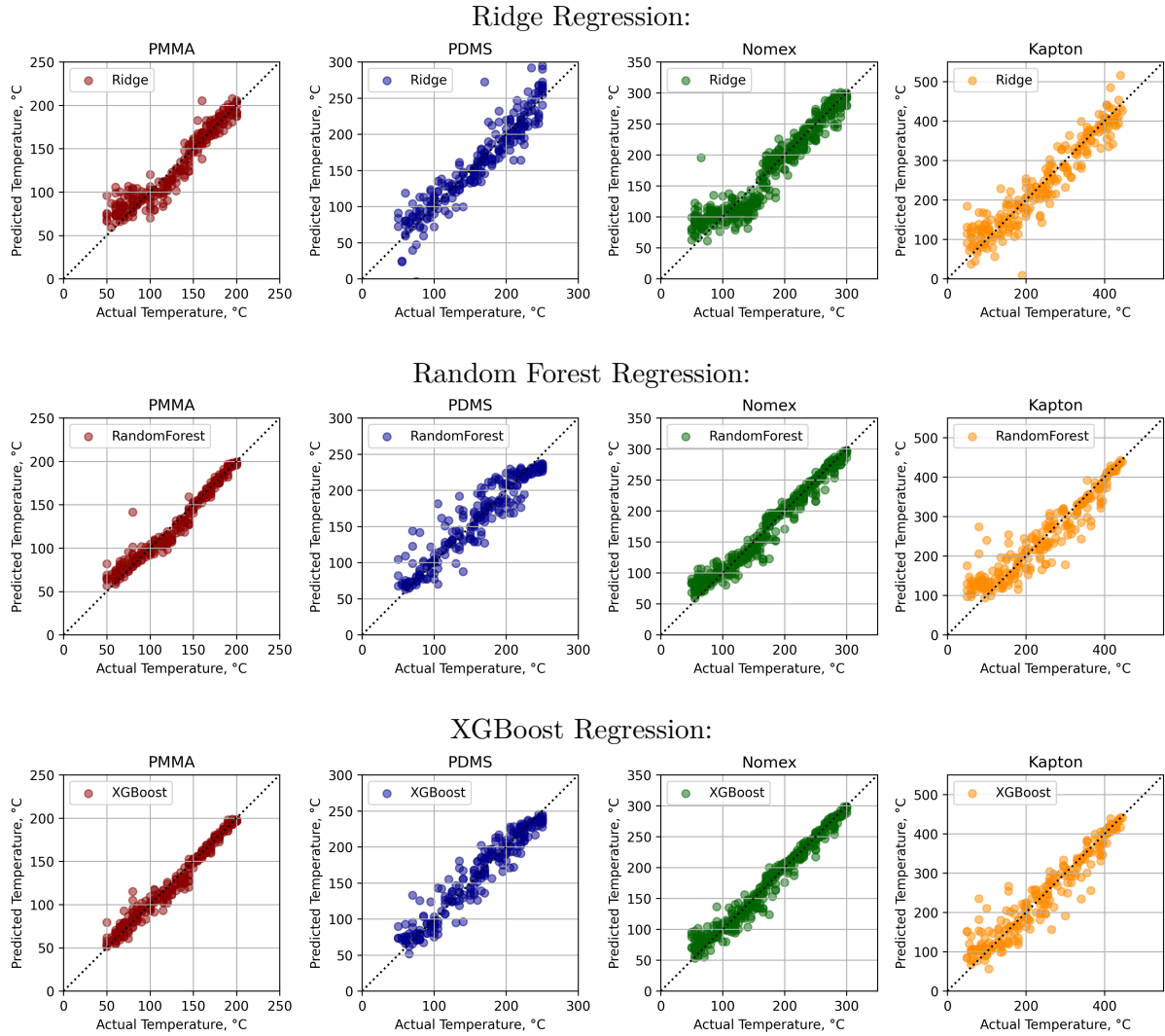


Figure 5.9: Parity plots showing predictions by ridge, random forest, and XGBoost regression against actual temperatures. All data originates from the previously unseen test set of the respective material, recorded by the sensor operated in temperature modulation. In part adapted from [149].

Table 5.7: Model performance metrics of the single-material test set, recorded by the sensor operated in temperature modulation.

Material	Regression Model	RMSE, K	MAE, K	MRE, %	R^2
PMMA	Ridge	13.20	9.94	10.35	0.91
PMMA	RandomForest	8.66	5.84	6.12	0.96
PMMA	XGBoost	7.51	5.30	5.33	0.97
PDMS	Ridge	20.18	15.32	12.02	0.88
PDMS	RandomForest	19.67	14.19	11.01	0.89
PDMS	XGBoost	16.03	12.40	9.81	0.93
Nomex	Ridge	21.43	16.52	14.59	0.92
Nomex	RandomForest	13.57	9.90	8.86	0.97
Nomex	XGBoost	12.18	8.70	7.67	0.97
Kapton	Ridge	46.20	29.47	19.03	0.85
Kapton	RandomForest	39.92	28.43	22.03	0.89
Kapton	XGBoost	35.23	24.70	17.66	0.91

Sensor in Temperature Modulation – Multi-Material Analysis

The resulting parity plots from the evaluation of the sensor operated in temperature modulation using the combined dataset, are displayed in Figure 5.10. The ridge regression model, trained with data from the temperature modulated sensor, clearly outperformed the model trained using data from the sensor at constant 300 °C. The vertical line at actual 25 °C is visible for all materials, but not as high, allowing for predictions from a lower TH of predicted temperatures on.

Improvements by the other two regression types are significant as well. Less scattering and less outliers are observable for the random forest regression displayed here, compared to parity plots obtained from the sensor operated at constant temperature. Concerning XGBoost, the predictions on PMMA show no major outliers and almost perfect linearity with a short vertical line at 25 °C. The PDMS data still shows scattering in predicted values, yet, impressively little, when keeping in mind the shallow slope and low sensor signal in the univariate analysis. The parity plots of Nomex show the greatest linearity, with a R^2 of 0.99 for the XGBoost regression (Table 5.8). The outliers could most probably be avoided, by more extensive hyperparameter tuning, or a larger set of data

for training. The predictions for Kapton show the same R^2 for random forest and XGBoost but lower errors for random forest in MAE and MRE.

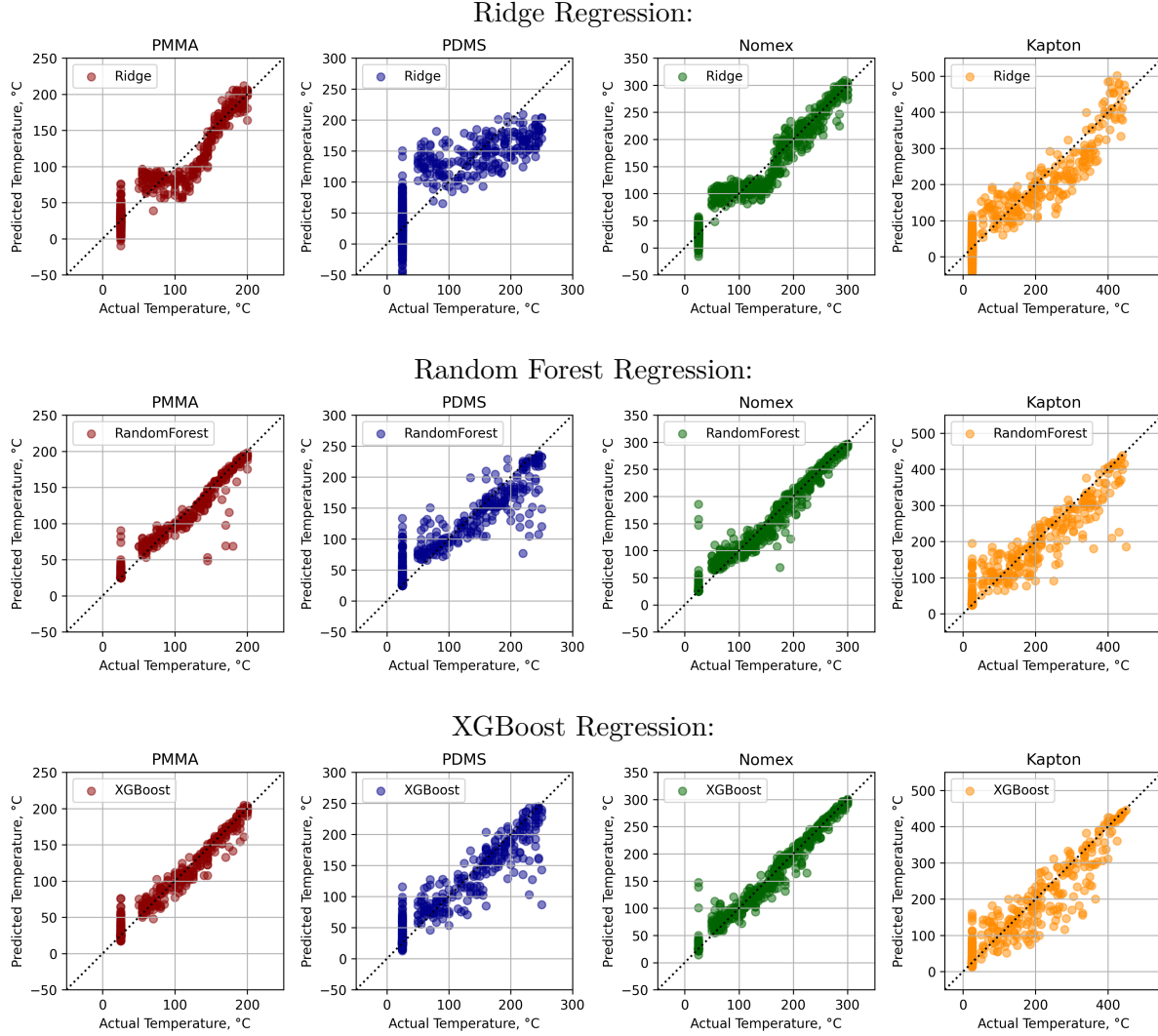


Figure 5.10: Parity plots showing predictions by ridge, random forest, and XGBoost regression against actual temperatures. All data originates from the previously unseen test set of the combined materials, recorded by the sensor operated in temperature modulation. In part adapted from [149].

Table 5.8: Model performance metrics of the combined-material test set, recorded by the sensor operated in temperature modulation.

Material	Regression Model	RMSE, K	MAE, K	MRE, %	R^2
PMMA	Ridge	13.99	10.37	29.60	0.92
PMMA	RandomForest	8.64	2.68	4.74	0.97
PMMA	XGBoost	6.52	2.74	5.83	0.98
PDMS	Ridge	30.38	22.20	62.93	0.73
PDMS	RandomForest	18.48	7.47	14.97	0.90
PDMS	XGBoost	16.25	6.94	14.20	0.92
Nomex	Ridge	16.77	12.57	28.65	0.96
Nomex	RandomForest	12.36	5.07	6.90	0.98
Nomex	XGBoost	9.97	4.22	5.52	0.99
Kapton	Ridge	33.24	24.42	68.28	0.89
Kapton	RandomForest	26.73	10.12	14.94	0.93
Kapton	XGBoost	26.30	11.24	19.28	0.93

In conclusion, the use of sensors in temperature modulation proves to highly increase the information gain compared to the sensor measuring simultaneously at a constant temperature. This increase in information does not always result in a decrease of error. While RMSE was chosen for model selection due to its stronger penalization of large errors, MRE provides a more intuitive and scale-independent measure, enabling better comparison across different materials. It is therefore exemplarily displayed in Figure 5.11 as a bar chart for the single material and multi-material analysis discussed previously. In the single-material analysis of PMMA, the sensor operated at 300 °C (const) shows higher MREs for all models. By using the sensor in temperature modulation (TMM 2), the errors could be decreased by almost half using ridge, and more than half with XGBoost. In contrast, the sensor operated at constant temperature yields very comparable MREs on the data of PDMS. For the predictions of Nomex, the use of temperature modulation improves all of the MREs, with the largest improvement for the XGBoost model. Kapton prediction shows the largest errors overall, explainable by shallow slopes and low sensor signals in the univariate analysis (see Figure 5.4). The sensor undergoing temperature cycles outperforms the sensor operated at constant

temperature, when employing ridge regression.

The fact, that in some cases the sensor in constant operating mode shows better performance than the sensor in modulated operation, can be explained by too much variation in features. Similar was the case for the small PMMA dataset in Section 5.1, which is reported in detail in [148]. Especially for large variation in the data, enough samples have to be recorded to explain and train the relation between the features and target value. The more complex the feature space (for instance by large variations in resistance values, the modulation itself, or the complexity of data), the more samples are needed to learn that relationship. The pixels resistances, when recorded at constant operating temperature, show a clear relationship to the material temperature and therefore deliver accurate predictions for the single-material analysis.

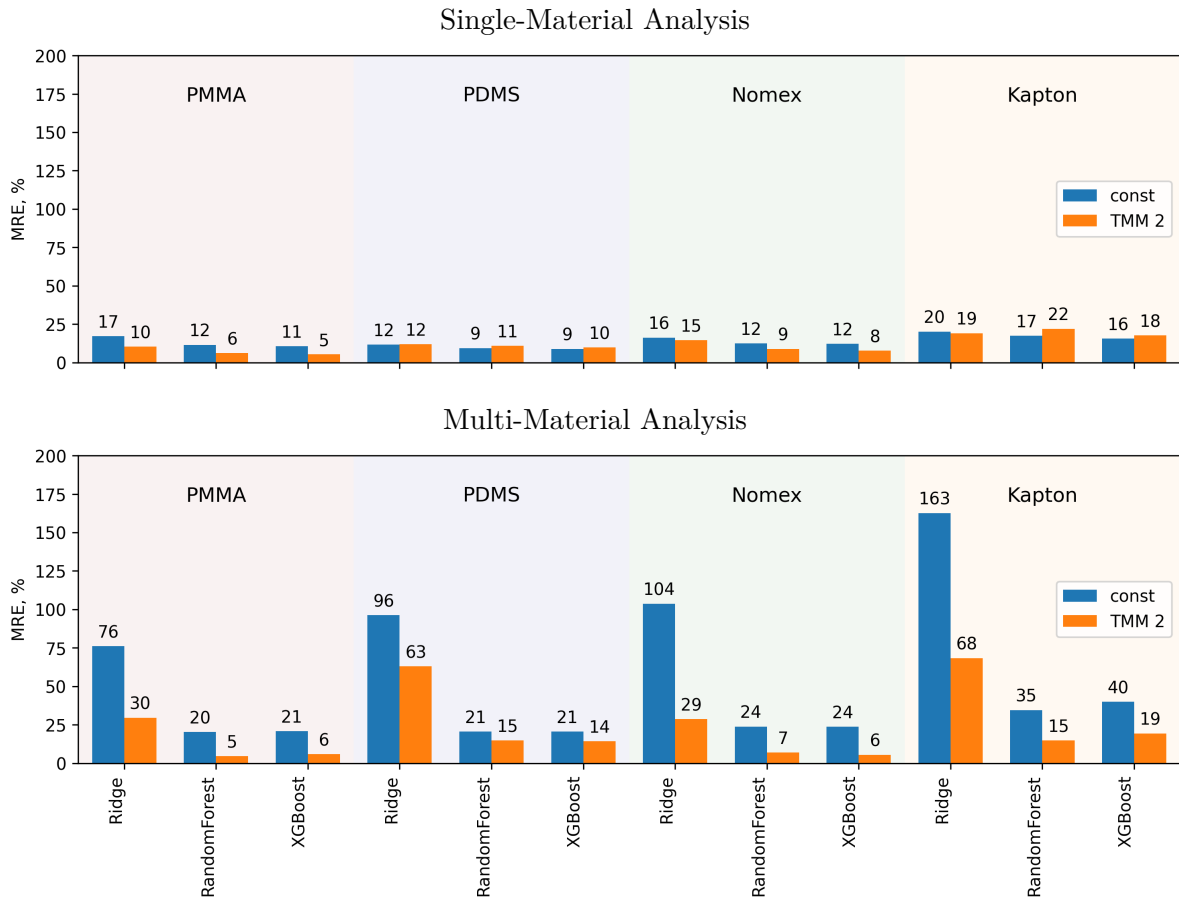


Figure 5.11: Comparison of mean relative errors.

All the MREs are lower for the cycled sensor in regard to the multi-material analysis (using the combined dataset). The lowest MRE is 5 %, for the PMMA data, using random forest, followed by 6 % for Nomex (XGBoost) and 14 % for PDMS (random forest and XGBoost). The lowest error for Kapton was obtained using the random forest regressor with 15 %. The reduction of errors, from constant temperature to temperature modulation in the combined-data regime, is significant, partly even exceeding performance in the single-material case.

The necessity of a larger dataset, explains the worse performance for some of the models, with the sensor in temperature modulation using the single material analysis in contrast to the multi-material analysis. The larger amount of data, when combining the materials, is beneficial in this case. Generally, one can conclude, that the tree-based models are better suited for this data, especially when non-linearity is expected.

Comparison of Operation Modes

In this study, six slightly different temperature modulations were employed on six SGP40 sensors, displayed in Figure 3.1, in 3.1. Figure 5.12 shows the error metrics, resulting from the single-material analysis, with the best model (by RMSE) trained individually per material. Figure 5.13 shows the results obtained when training one model with the same parameters across materials, using the multi-material dataset. The panels include all temperature modulations and the results obtained from the sensor operated at constant 300 °C. TMM 2 was chosen as a representative, because, as shown in Figure 5.12, most of the case yielding the lowest errors. Nevertheless, sometimes the sensor on constant operation mode outperformed the modulated ones. This could be due to the aforementioned complex feature space, needing additional data to map it to the correct output.

5.2 Predicting Material Temperature from Outgassing

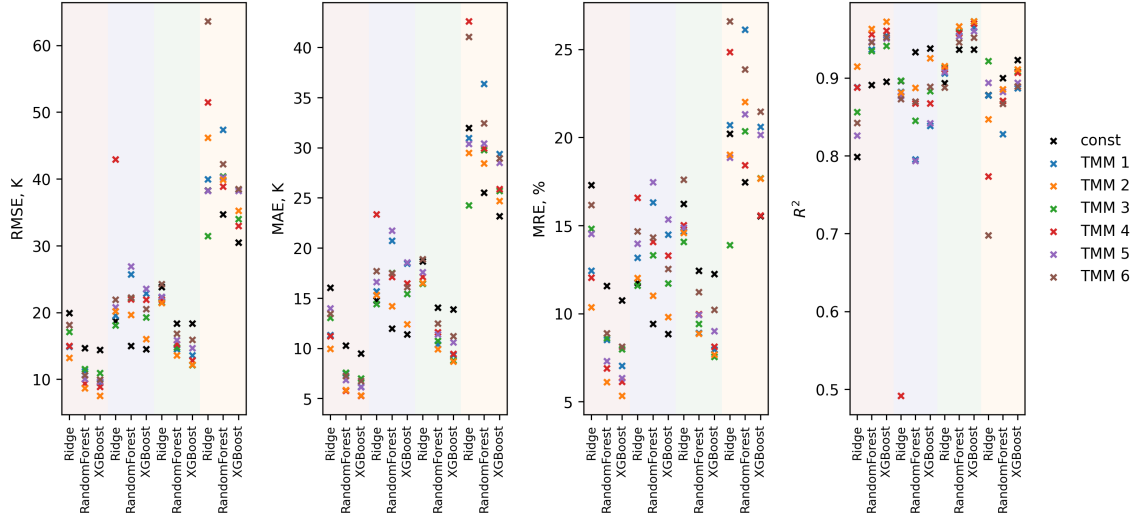


Figure 5.12: Comparison of results, obtained for different operating modes on the single-material dataset. Per panel, from left to right: PMMA, PDMS, Nomex, Kapton.

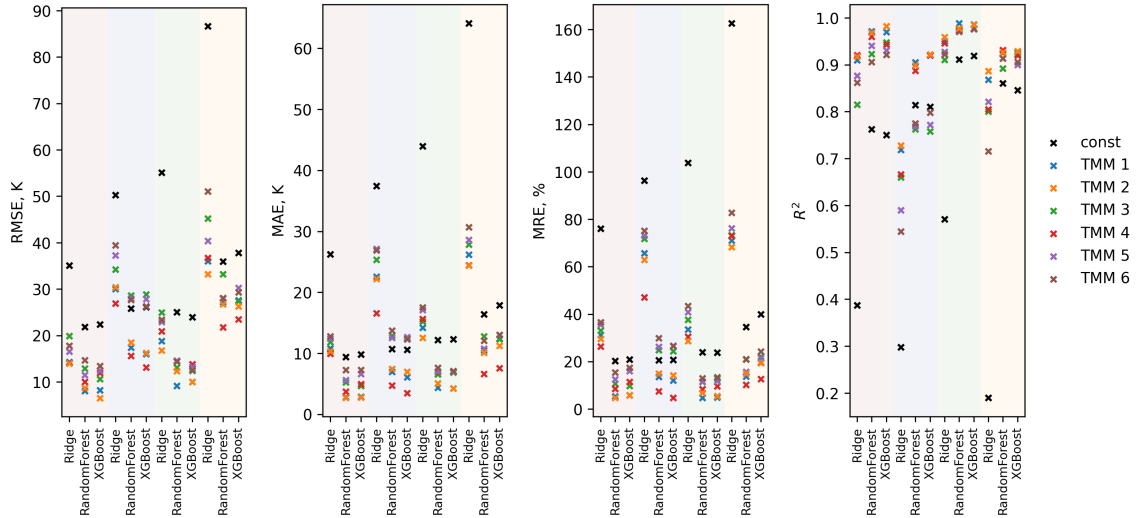


Figure 5.13: Comparison of results, obtained for different operating modes on the full dataset. Per panel, from left to right: PMMA, PDMS, Nomex, Kapton.

Besides TMM2, which was one of the best performing, according to Figure 5.13, TMM4 and TMM1 show particularly low errors and high values for the coefficient of determination. Nonetheless, it is impossible to be set on one single modulation, performing best for all materials in this dataset. Effort was undertaken to identify the reasoning behind good performance, to improve the modulation for each application.

In previous works [113, 131] and from unpublished investigations using SHapley Additive exPlanation values*, the middle of the temperature modulations and the lower temperatures were found to often show a large influence on the prediction. Nonetheless, the performance of individual features is highly dependent on the target analyte, the environment, as well as the machine learning model utilized. The empirical approach of using several sensors, operated in different modulations, is the preferred, since the parameters decisive of good predictions are yet to be identified and tuned accordingly. Additionally, one single step of the modulation cannot simply be isolated, as the sequence influences the reactions on the sensor and their kinetics.

It should be noted, that the sensor-to-sensor variation can influence the performance as well. However, the fact that the best modulation differs for the four materials tested, suggests the dominance of the modulation and implies the potential of further performance improvement by the use of tailored temperature cycles.

Taken together, the findings show, that operating the sensor under temperature modulation yields improved performance (given sufficient data availability), making temperature prediction and material distinction feasible, as supported by the corresponding errors and parity plots.

* Information on the method can be found in [152]

6 Sample Analysis Using GC-MS

The initial analysis, using TGA-MS, delivered sparse information about the outgassing species. To support the findings obtained with the SGP40 and potentially identify temperature markers for threshold selection (as explained in 2.1 and visualized in Figure 2.1), additional GC-MS measurements were conducted.

Three samples (A, B, and C) per material (PMMA, PDMS, Kapton, and Nomex), of approximately 0.5 g were prepared and filled into vials. To identify the outgassing species, coupled to a certain temperature, each sample was incubated at 100 °C for 20 minutes, before 500 µl of headspace was injected from the vial, using a 2.5 ml autosampler syringe. After the injection, the vial was purged with helium for 30 seconds to flush the headspace, before it was closed again, heated to 150 °C, and the process repeated for this and a third temperature of 200 °C. Between each injection, several blank samples of laboratory air were measured to detect and prevent carryovers.

To imitate the conditions of the measurements conducted in the ASTRA, a second series of measurements was executed: 500 mg of sample was heated to 200 °C for 20 minutes and six samples of the headspace collected manually, while ensuring pressure compensation by injecting air with a gas tight syringe. This led to a dilution of sample in the GC-MS of approximately 1:10, compared to the first measurement series. Each vial containing a subsample was heated to either 30 °C, 60 °C, or 100 °C for 20 minutes, before injection. In the following, chromatograms are presented using a consistent detector signal scale to ensure comparability. Mass spectra are normalized to relative intensity and peaks with intensities below 1 % are excluded from the experimental spectra to improve visual clarity.

PMMA

The clear temperature dependence in the amount of outgassing is depicted by the chromatograms in Figure 6.1 for three samples of heated PMMA. At 100 °C, only a very low peak can be observed at a retention time of 34.40 minutes, which increases with temperature. A second peak, at the retention time of 64.30 minutes, appears in the 150 °C chromatograms and dominates in intensity at 200 °C. A third dominant peak, eluted after 56.97 minutes, is observable in the 200 °C measurements as well. The three peaks, annotated in the right panel, showing the measurements at 200 °C, were selected as potential temperature markers. Two of them already show significant height at 150 °C, allowing for a detection between 100 °C and 150 °C. The findings agree with the increase in sensor signals of the SGP40, at about 125 °C. Differences in signal intensity are observable between the three samples A, B, and C. However, the peaks occur at similar retention times.

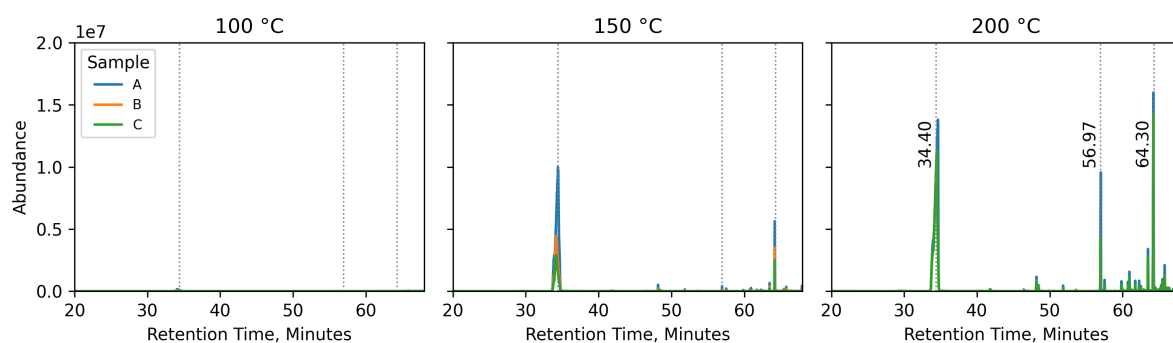


Figure 6.1: Temperature-dependent outgassing of PMMA: comparison of chromatograms at 100 °C, 150 °C, and 200 °C.

Based on the reference spectra from the NIST library, the mass spectra of the selected peaks were identified as: MMA, 1-dodecene, and 1,6-dimethyl 2-methyl-5-methylidenehexanedioate. In Figure 6.2, the normalized detector intensity is displayed as a function of the mass-to-charge ratio for the experimental spectra, mirrored to the matched reference. MMA, 1-dodecene, and 1,6-dimethyl 2-methyl-5-methylidenehexanedioate align with the mirror plots, with a few additional masses in the experimental spectrum.

The monomer MMA, which is already measurable in small quantities at 100 °C, is described in literature as an outgassing species of PMMA, detected at 90 °C [153]. It is a logical candidate regarding the synthesis of PMMA. Additionally, it is expected to

occur across manufacturers and applications. According to the TGA-MS measurements, the degradation of PMMA starts at roughly 280 °C, therefore the measured monomer is likely residual reactant instead of an early degradation product.

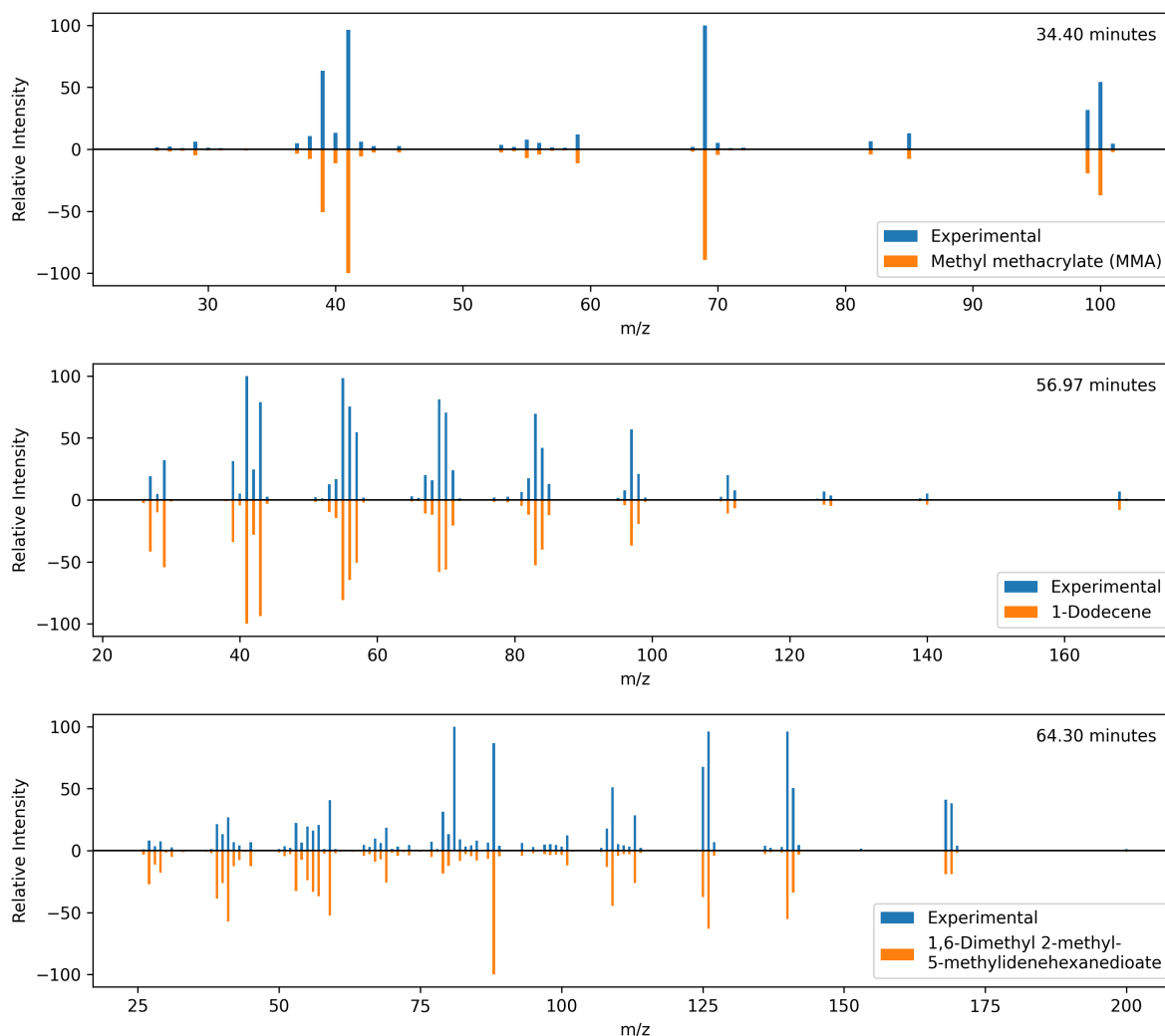


Figure 6.2: Mirror plots of experimental mass spectra against selected NIST-database spectra. The experimental spectra were obtained from the chromatograms of PMMA at 200 °C.

While one of the use cases of 1-dodecene is general polymer production [154], it can not be excluded that it formed as a secondary product during PMMA heating or during the GC-MS analysis. The substance 1,6-dimethyl 2-methyl-5-methylidenehexanedioate is an unexpected finding that could not be directly linked to the production of polymers. It could be a secondary product which formed in the column from different fragments, or

a misidentification. Nonetheless, the use as additive or processing agent cannot be fully excluded.

Additional species, detected at 200 °C, could be considered as additional temperature markers. However, their low abundance in comparison to the dominant peaks reduces their relevance in regard to the sensing experiments.

The chromatograms of the subsamples heated to 30, 60, and 100 °C revealed only MMA measurable in a significant detector intensity. Possible condensation of analytes by manual sampling within the syringe and the 1:10 dilution of the initial concentration have to be considered. Nevertheless, given the experimental data, the sensor most likely measures mainly MMA when distant from the sample.

PDMS

In contrast to the lack of signal by the four pixels of the SGP40, the chromatograms in Figure 6.3 show a clear increase in abundance with increasing temperature. An assignment of the signals using the database delivered a variety of different siloxanes as candidates. The mass spectra of the two dominant peaks are shown in Figure 6.4, mirrored against their respective best-matching reference spectra. Even though siloxanes can originate from the column of the system, the intensity of the peaks, absent in the other samples and absence in the blanks, support the findings.

Cyclic as well as linear volatile siloxanes are known to form as rearrangement products from PDMS under certain conditions, or outgas as residues from the finished polymer [155–157]. As a result of the variety and the frequency in the application of siloxanes, like PDMS, there is an omnipresence of these species and their fragments in indoor air [158]. This is equally true for the air on the ISS, where the presence of these species poses challenges in the removal of soluble degradation products during water purification [159–162]. Similar to the Maximale Arbeitsplatzkonzentration - maximum workplace concentration (MAK) [163], the health of the occupants of the ISS is regulated by Spacecraft Maximum Allowable Concentrations (SMAC) values [164].

SMOX-based sensors can become poisoned from exposure to siloxanes, as extensively reviewed by Staerz et al. [165]. Thus, the SGP40 (as its predecessor), is equipped with MOXSens® Technology, making it more robust against siloxane contamination [62, 166, 167]. According to Rüffner et al. [62] on the SGP30: “This is achieved by a combination and optimization of the sensing material, operation mode, and the on-chip evaluation

of multiple signals from different sensing elements“. While this feature is valuable for the longevity of the sensor, it explains the absence of significant response in the measurements in Chapter 5. Because of low sensor signal and low detector abundance, measuring subsamples was omitted for this material.

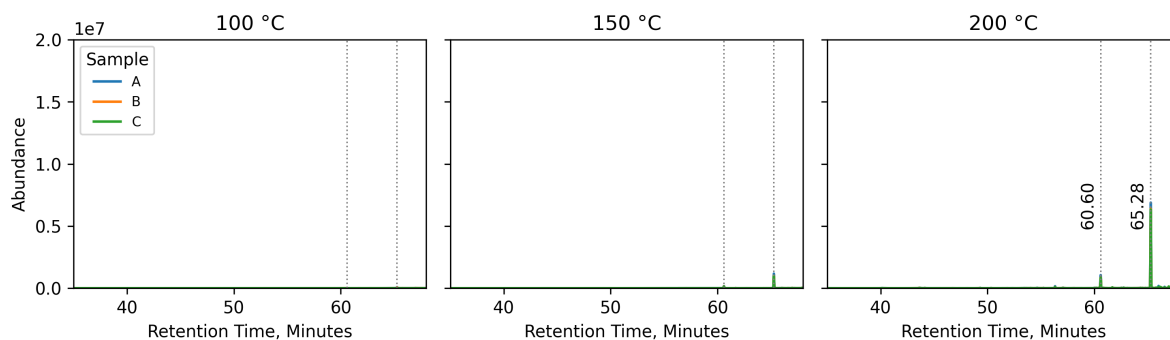


Figure 6.3: Temperature-dependent outgassing of PDMS: comparison of chromatograms at 100 °C, 150 °C, and 200 °C.

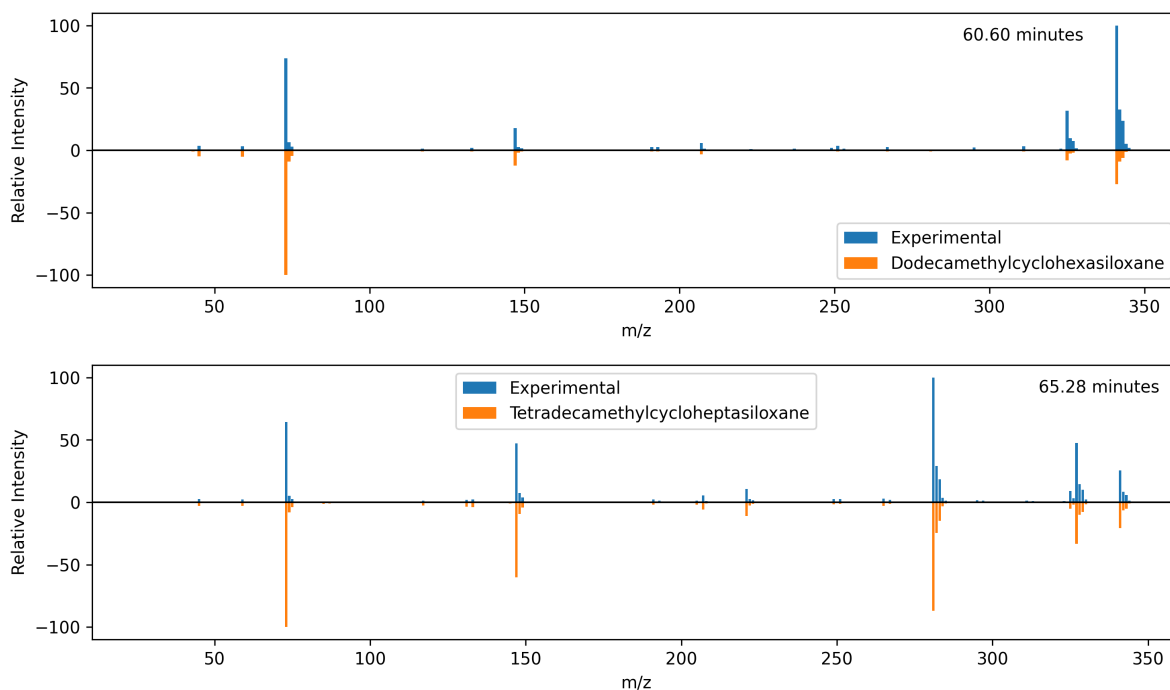


Figure 6.4: Mirror plots of experimental mass spectra against selected NIST-database spectra. The experimental spectra were obtained from the chromatograms of PDMS at 200 °C.

Nomex

Based on the detection using the SGP40, Nomex should deliver visible peaks at roughly 155 °C. Nevertheless, several peaks can be clearly identified at 150 °C in Figure 6.5, which could be attributed to the material temperature in the tube furnace being slightly lower than the temperature below the glass boat, where the thermocouples are located. Another explanation could be that the colder gas plume (not directly at the heat source) contains less species.

The intensity of the four dominant peaks only slightly increases towards 200 °C, compared to the initial increase from 100 to 150 °C. The corresponding mass spectra are depicted in Figure 6.6, with the suggested reference from NIST. The spectra of the species show well alignment with the experimental spectra. Based on the peak pattern in the chromatograms at 200 °C a homologous series can be assumed.

In agreement with the findings on the fabric Nomex, aliphatic fatty alcohols of different chain length, including undecanol, dodecanol, and their ethoxylates, are used in different processes of fabric finishing [168, 169]. Part of the signals, identified as the corresponding aldehydes undecanal and dodecanal, may result from partial oxidation during the measurement (e.g., in the injector or transfer line). Nonetheless, long-chain aldehydes can also be added intentionally in the textile finishing formulations or arise from oxidation of alcohols during processing or storage.

No significant analyte abundance was observed in the Nomex subsamples, consistent with the initial 100 °C measurements.

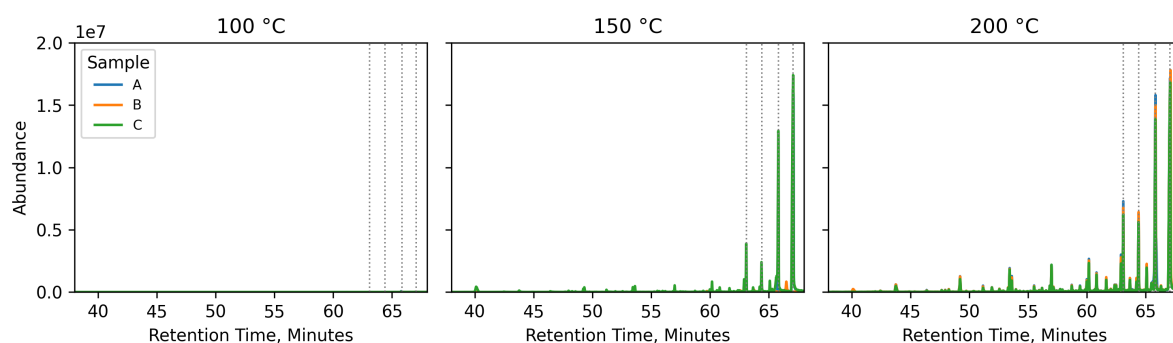


Figure 6.5: Temperature-dependent outgassing of Nomex: comparison of chromatograms at 100 °C, 150 °C, and 200 °C.

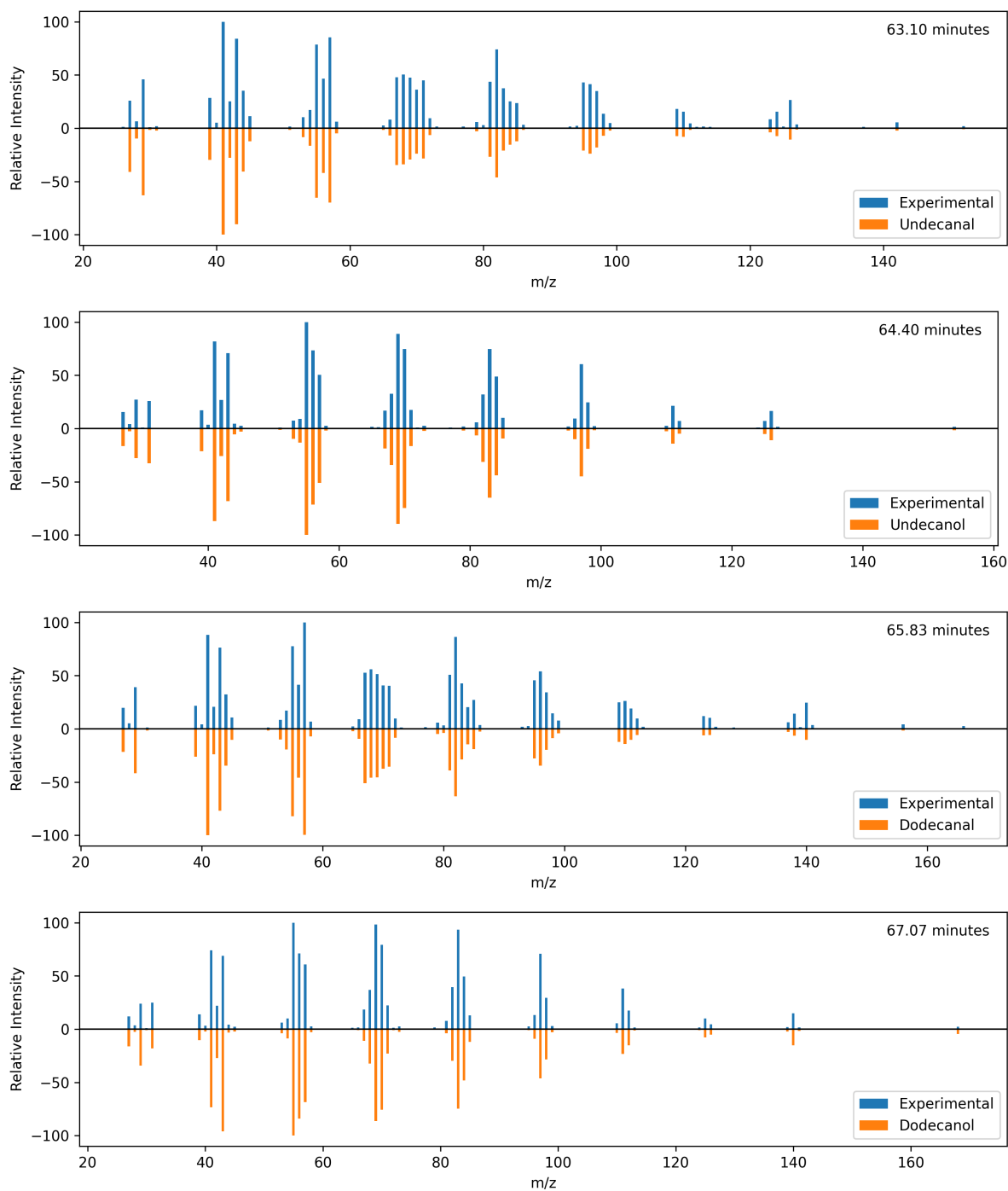


Figure 6.6: Mirror plots of experimental mass spectra against selected NIST-database spectra. The experimental spectra were obtained from the chromatograms of Nomex at 200 °C.

Kapton

Only minor peaks, hardly distinguishable from the background noise, could be detected for Kapton at 100 °C, 150 °C and 200 °C (see Figure 6.7). By adjusting the scale of the detector intensity, increasing signals can be observed for increasing temperature (Figure 6.8). The two peaks at the retention times of 34.40 minutes and 56.97 minutes for A at 100 °C, were identified to originate from the prior measurement on PMMA. Because of the sensor not being able to measure the low concentrations, emitted at the three temperatures reported here, the compounds were not further analyzed. Due to the limitation of the incubation oven to 200 °C, the analysis could not be expanded to temperatures at which the SGP40 is able to detect the outgassing reliably. For the same reason, measurements of subsamples were not conducted.

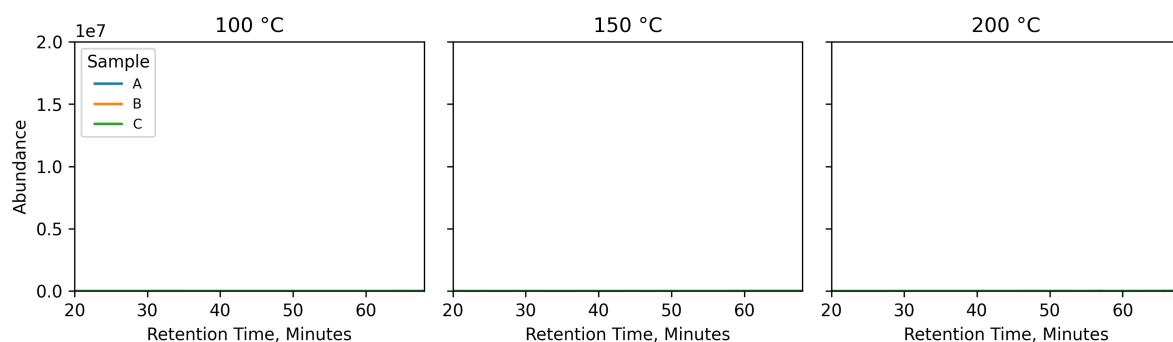


Figure 6.7: Temperature-dependent outgassing of Kapton: comparison of chromatograms at 100 °C, 150 °C, and 200 °C.

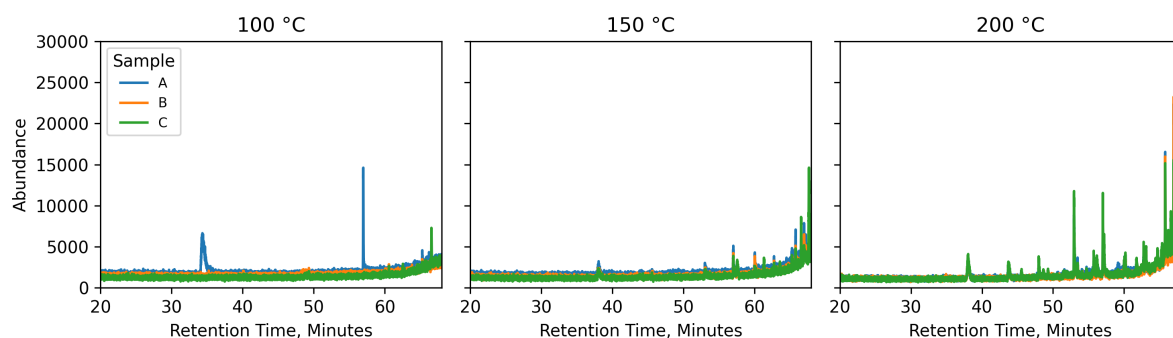


Figure 6.8: Temperature-dependent outgassing of Kapton: comparison of chromatograms at 100 °C, 150 °C, and 200 °C with adjusted y-scale. The substances eluting at 34.40 minutes and 56.97 minutes in A, at 100 °C, were carried over from the previous PMMA sample.

In summary, for all materials, an increase in outgassing can be observed with an increase in temperature. This is the prerequisite for pre-ignition detection using SMOX-based sensors. The species detected are not necessarily additives, but monomers or substances added in later processing steps. The sensor showed insignificant response to PDMS, while the chromatograms revealed measurable species, though in low abundance. A minor increase in detector abundance with increasing temperatures was found for Kapton, yet it is expected to amplify in higher temperature regimes, as observed in the sensor measurements.

All dominant species identified are unique and therefore explain the ability of the SGP40 to differentiate between the materials. Although beyond the scope of this work, further evaluation and validation of the gas signatures would support the future development of sensors containing of materials specialized for this application.

7 Sensor Network-Based Gas Source Localization and Distribution Analysis

The use of SMOX-based SGP40 sensors for early detection of heated polymers was tested and evaluated in Chapter 5 *Temperature Predictions*. In this chapter, the ability of the sensors concerning GSL is investigated, as the last objective addressed in this work, based on [134]*.

A CSG, consisting of 32 SGP40 sensor arrays (operated at 350 °C), was constructed as described and visualized in 3.3. The source location was fixed in one out of three possible positions to enable classification based on 15 measurements of PMMA, which was selected to represent the modified polymers. The material was chosen based on the comparably high outgassing and the promising amount of measured MMA, even at low subsample temperatures, identified via GC-MS. Measurements were conducted using approximately 200 mg of sample and repeated five times per furnace position. Each of the runs was executed in the same manner: the sample was inserted into the furnace (on the previous day) by using a marked glass rod to push the boat, loaded with the sample, into the correct position. On the day of the measurement, the start time was documented and the furnace manually set to 8 V (2.8 A), reaching approximately 205 °C after a total of 30 minutes. After that period, the system was vented and when completely cooled down, the sample exchanged for a fresh one in preparation for the following day. In each position, a total of five samples were measured. Additional three samples with lower sample mass were measured in the same manner, to compare the results and assess the generalization ability of the model in terms of sample mass/concentration.

* Illustrations reprinted and text adapted from L. Schynowski, F. Meyer, U. Weimar, N. Barsan, Exploring pre-ignition source localization using a 3D network of semiconducting metal oxide gas sensors, *Sensors and Actuators B: Chemical*, 2026, 467: 140442, © 2026 The Author(s), licensed under CC-BY 4.0 (<https://creativecommons.org/licenses/by/4.0/>).

7.1 Sensor Signal Shapes

Large amounts of information about the gas plume spread, and therefore optimal positioning of the sensor, can be extracted from the 1920 individual time series. In addition to the 30 minutes of furnace operation, five minutes of baseline were added, then the raw data, subject to only baseline correction and smoothing were evaluated.

As a representative, pixel 2 was chosen, showing the largest response to PMMA (based on the previous results). The sensor signals, calculated as the ratio between each data point by the mean of three minutes baseline (before the activation of the tube furnace), were smoothed with a window of five, displayed in Figure 7.1. The sensor signals are color-coded according to the position of the furnace. For some sensors, the difference in source position is visible by the height or shape of the sensor signal over time. For example, a14 shows a separation in height at the end of the time series, while in b32, position 2 can clearly be distinguished by the shape of the orange sensor signals. Some sensors show strong outliers, for example a'22, with a sharp local maximum for one of the curves, or a21, with one time series in position 1 exceeding all other values.

Based on the sensor signal shapes, some initial identification of the positional dependence of sensors, with respect to their ability to discriminate between source positions, can be assumed. Some sensors show distinctive shapes in dependence of the position, e.g., b33, b32, b23, and b13, arranged in a *T* formation. The sensor signals of position 2 for these sensors are **going through a maximum**, possibly passed by the high concentration plume, before it mixed into the surrounding atmosphere. The plume must move non-symmetrical, according to this first observation, with a larger positional dependence in outgassing towards side b. These sensors seem to record especially high concentration for the source in position 2, accompanied by large fluctuations and therefore uneven shapes. Similar can be seen for the sensors on side b', indicating dominance of positional dependence rather than sensor-to-sensor variation. b'23 shows some similarities to its neighbor b23, yet position 2, in this case **approaches a plateau**, indicates that the plume is already well mixed when reaching the sensor. The sensor signals for the other two source positions, recorded by b'23, are **ever increasing**, as the concentration of the plume seems to be in this position. Based on these three categories of signal shapes, one can already make assumptions on the performance of a sensor, tied to its position. Hence, the signal shape and height should be identical for the same source location and different between source positions. For many sensors, a visual distinction is difficult or impossible, suggesting that they may not perform well in separating source location.

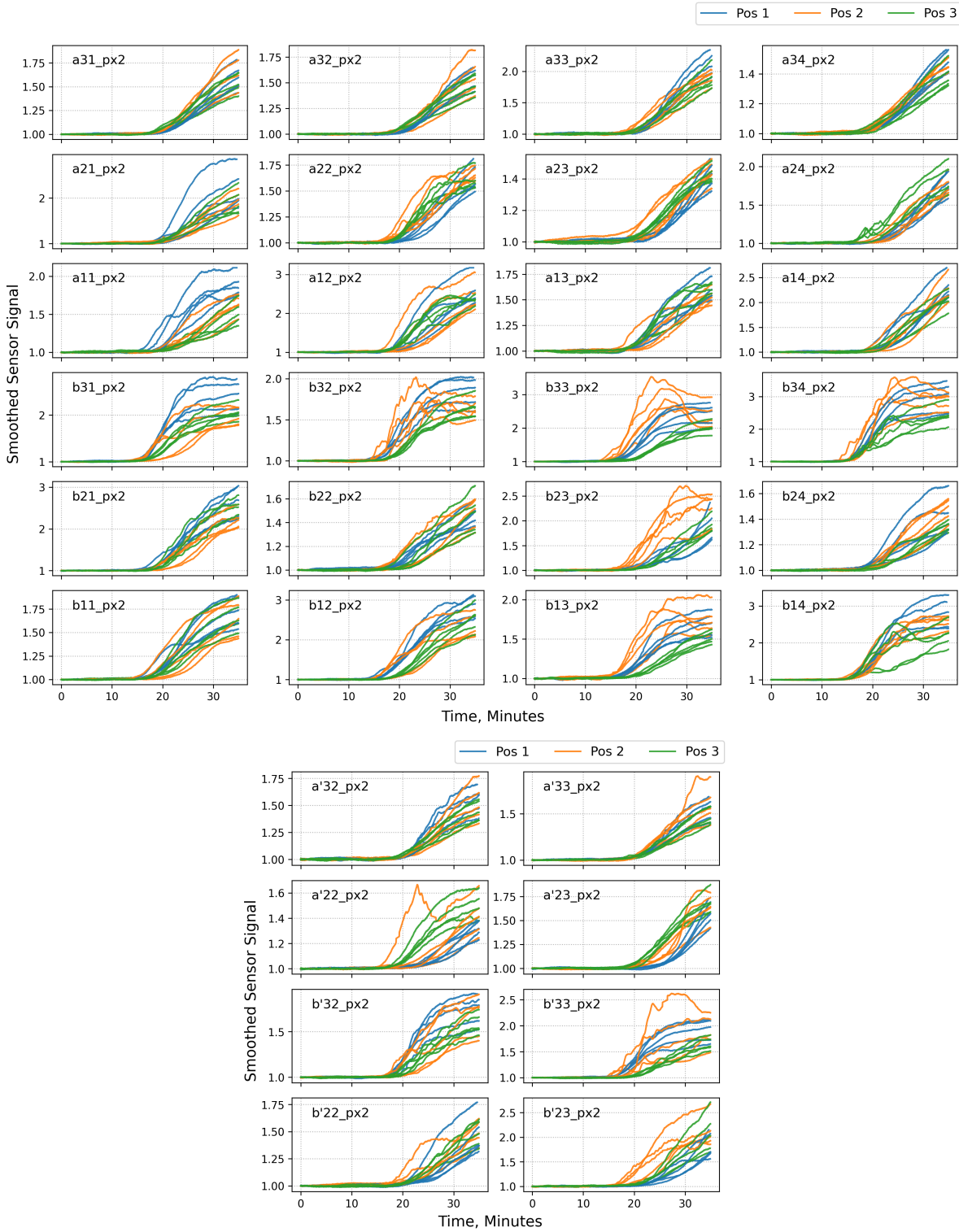


Figure 7.1: Sensor signals of sensors a, b, a', and b' pixel 2, smoothed with a rolling mean of five seconds, equal to five data points. The source location can be identified by color-coding. Reprinted from [134].

The sensor signals were further processed individually as z-scores, obtained by subtracting the mean and dividing the standard deviation. By transforming the sensor signals, the values become centered around zero and more comparable, when different in magnitude. The change from raw to z-scored values are visualized on two examples of *good* (b32) and *bad* (a12) separability, according to the before established shape categories. b32, as visualized in Figure 7.2, shows a difference in curve shapes for position 1: **reaching a plateau**, position 2: **going through a maximum**, and position 3, with a late onset at approximately 17 minutes and a curve shape that is **continuously increasing** with a shallow slope. After z-transformation, the sensor signals are more bundled and even easier to distinguish in shape. The sensor in position b32 shows clear distinction in curve shape, dependent on the source position. Therefore, z-transformation removes differences in signal amplitude, while preserving the shape of the time series.

The variation observable in the individual time series is low for position 1 and 3, while large in position 2. It can be assumed, that the structure is related to the concentration differences in the plume and the sensor therefore resolves the local differences when in the turbulent, high concentrated gas stream. As a result, sensors which are passed by in early plume stages should show this variability, while sensors further from the source, should exhibit smoother signals as they see well-mixed plume with less local gradients.

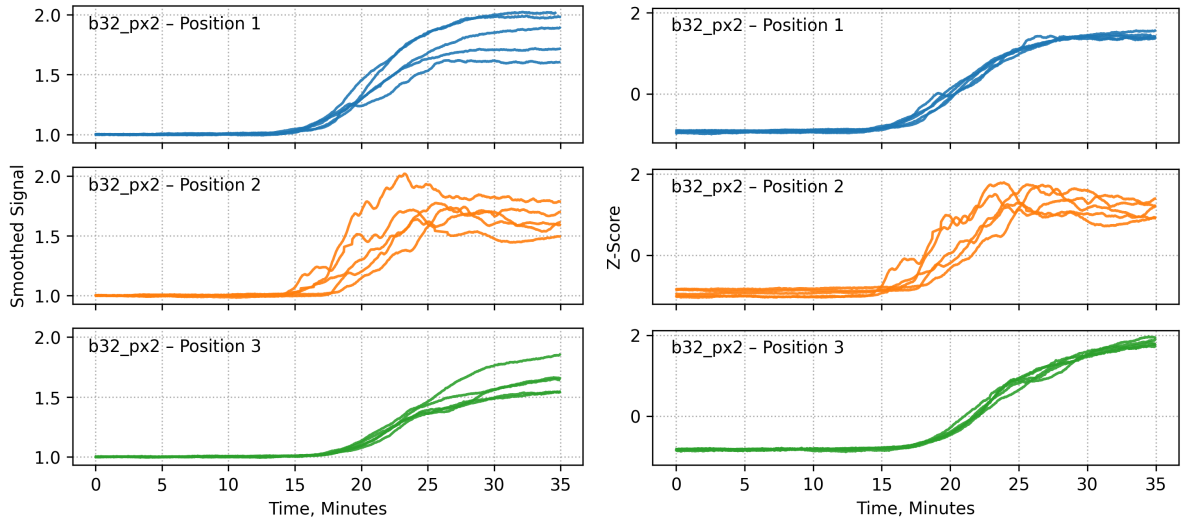


Figure 7.2: Processed sensor responses recorded with b32 pixel 2 for three furnace positions. Left: Raw sensors signals, right: z-scores. Reprinted from [134].

The sensor in Figure 7.3, positioned at a12, exhibited mixed signal shapes for the same source position. In all three classes, two measurements do not align with the remaining three. Such variation could have been caused by slight difference of the sample position or distribution inside the tube furnace, yet not prominent in other sensors (e.g., b32). The calculated z-scores in the right panel show the same trend of misalignment. In addition, higher variation in position 1, close to the sensor cannot be observed, contradicting the findings with b32.

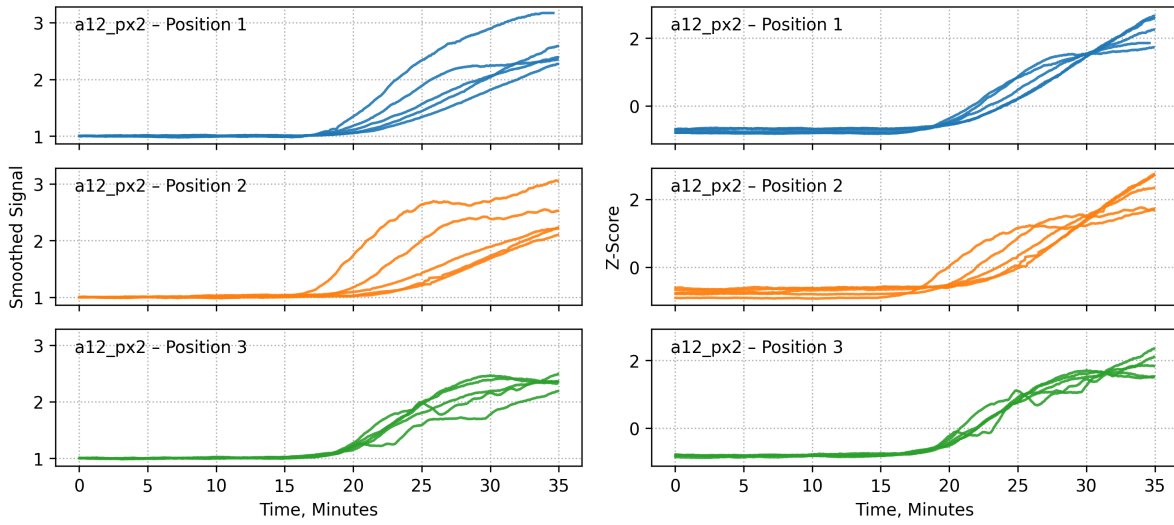


Figure 7.3: Processed sensor responses recorded with a12 pixel 2 for three furnace positions. Left: Raw sensors signals, right: z-scores. Reprinted from [134].

In conclusion, the sensors show large differences in signal shape, related to their position. Based on local similarities between sensors, it can be deduced, that the signal shapes stem from real effects related to the local plume, rather than sensor-to-sensor variations. Z-scoring has the potential to improve the separability, while in some cases removing the amplitude of signals might lead to loss of important information.

7.2 Variation in Plume Movement

In order to report on the repeatability and variation of the measurements, the recordings in identical source placement were compared using the untransformed sensor signals of pixel 2. For each individual measurement, the correlation matrix was first calculated, then the standard deviation σ and the mean μ across all five correlation matrices (with the source in the same position) obtained, per matrix element. From the correlation matrices per source position, the coefficient of variation (CV) was calculated per matrix element as in Equation 7.1. The resulting three CV-matrices are displayed in Figure 7.4. Based on the visualization, changes in plume movement during measurements of the furnace position can be compared.

$$\text{Coefficient of Variation} = \frac{\sigma}{\mu} \cdot 100\% \quad (7.1)$$

The heat map for position 1 suggests some variation, yet there is no sensor position which is especially susceptible to the changes. In position 3, even less variation can be observed overall, except for the two sensors b14 and b34. When comparing the heatmap to the respective panels in Figure 7.1, the sensors show two time series, which differ from the other three green curves. Naturally, such differences occur due to variations in the plume, likely caused by change in the exact position of the tube furnace, the boat inside the furnace, and distribution of sample.

Using the CV as a measure of variability and therefore absence of repeatability, the figures suggest much higher variability for the plume in source position 2, which agrees with the observations from Figure 7.1 and the findings comparing a12 and b32. When comparing the total sum of matrix elements for the positions 1-2-3, the result 3553-7205-2260 clearly reveals the more extreme variation in 2. It is governed mainly by the sensors b32 and b33 with contributions from others like b13, b34, and b'33. The CV, obtained with the remaining three pixels, shows similar trends, as can be seen in Figure 9.3 in the *Appendix*.

The larger amount of fluctuation in the signal shapes categorized as **going through a maximum**, explains the higher variability for certain sensors in the CV-matrices. It can be assumed, that the plume has high concentration differences and is moving turbulent when it passes a sensor in an early stage. Thus, the sensor records the local concentration gradients.

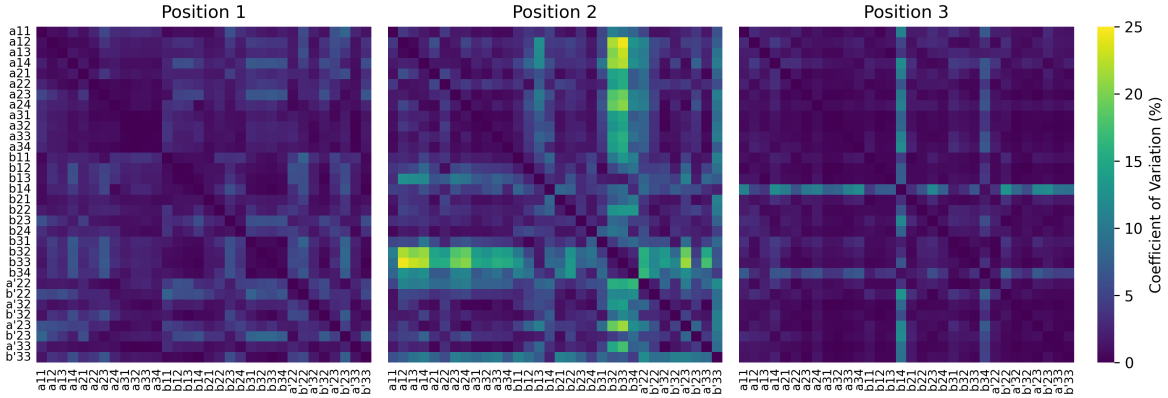


Figure 7.4: Matrices showing the coefficient of variation of pixel 2, calculated per source position respectively. Reprinted from [134].

Generally, higher variability in signal shape is measured for source position 2, therefore the configuration of the setup has to be taken into consideration. If the source is in the center, a larger number of degrees of freedom might be available to the plume, which could be a possible explanation for the observed differences.

As shown in Figure 7.5 a), the plume can move upwards in any of the available positions. When in 1 or 3, as visualized in Figure 7.5 b), the plume likely moves away from the source along the horizontal Z-axis (either plus or minus) and in part down along the glass walls. When the source is in position 2 (Figure 7.5 c)), there are more different directions the plume can move toward (in early as well as in late stages) leading to increased variation.

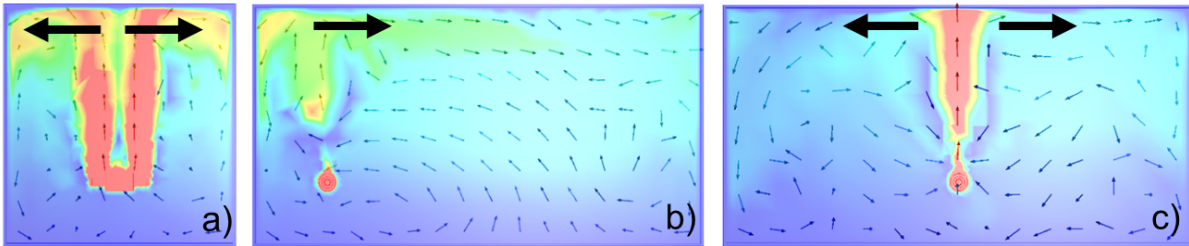


Figure 7.5: Illustration qualitatively describing the plume movement and temperature by color code (simulated using Autodesk CFD 2026). The hot areas are displayed in red, gradually changing through orange, green and yellow to cold areas in dark blue. The small arrows indicate velocity directions, while the black arrows indicate the dominant directions of plume movement. The view from the short side is visualized in a), equal for all positions. b) displays source position 1 and 3, while c) visualized the source in position 2. Reprinted from [134].

Local trends, like the high difference between classes by signal shape in the T -zone on side b, suggest advantageous sensor positions. However, without a quantitative measure, they are difficult to compare. Additionally, the selection of only one pixel allows for only one fourth of the available data to be compared at once. As the full dataset cannot be efficiently evaluated visually, the similarity of the signals was quantified and a classification performed using k-NN, as reported in the following.

7.3 Signal Alignment and Source Localization

In order to investigate the core methodology, DTW and k-NN were employed. In contrast to more advanced and complex deep learning approaches, these methods offer greater transparency and produce more easily interpretable results. Using DTW to obtain a single value, representing the similarity between two time series, a distance matrix was created, which then served as data for conducting k-NN using leave-one-out (LOO) cross validation.

The DTW-distances were calculated for each individual time series, treating each pixel of the SGP40 as an individual feature (1920 time series from 15 runs and 32 sensors with 4 pixels). The cost sum, obtained along the optimal warping path of each combination of runs, was calculated as the DTW-distance per pixel. An example is provided in Figure 7.6, using two runs (one obtained during the source in position 2 and one for position 3), recorded by pixel 2 in b32. In the left panel, the time series are compared (shifted on the vertical axis for visual clarity), matched by the DTW algorithm, with an unconstrained warping window (see *Time Series Analysis using Dynamic Time Warping* for more information). On the right panel, the resulting local cost matrix for the two time series is displayed in a heatmap representation, with the optimal warping path in red.

By averaging across all features, the 15×15 distance matrix was obtained, containing the average distances between each combination of runs, using information of all sensors. With a warping window of 20, this procedure was conducted twice: on the raw sensor signals, and the z-transformed data. Using $k=1$, in k-NN with the three source positions as classes, the untransformed data yielded 93% accuracy and the z-scored 100% accuracy after LOO cross-validation. The improved accuracy achieved with the z-scored data indicates, that the class-distinguishing-feature is the signal shape, rather than the amplitude.

Based on these results, it can be concluded, that the sensors, as distributed, are capable of correctly identify each class, when appropriate pre-processing via z-transformation is applied for the combination of DTW with k-NN. While this confirms the feasibility of gas source localization in the reported configuration, thereby addressing the final research question posed in this work, the following sections examine: the variation per sensor across source positions, the effect of sensor placement, and the potential of generalization to smaller sample masses as well as the constraints and limitations of the present experiment.

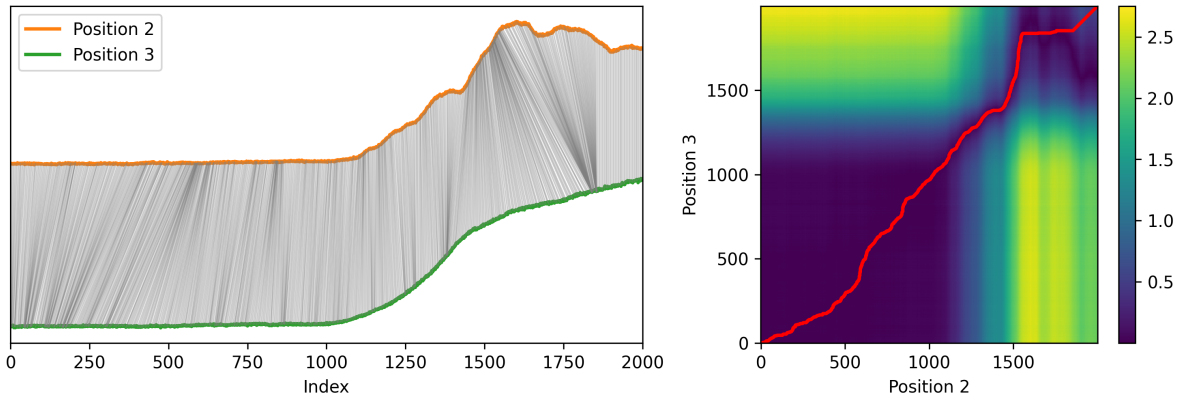


Figure 7.6: Signal alignment using dynamic time warping on two exemplary measurements by pixel 2 of b32. Left: time series alignment of the two vertically shifted time series with grey lines indicating the warping path. Right: heatmap representation of the local cost matrix with optimal warping path in red. Reprinted from [134].

Measurement Variability by Distance

In addition to the discussion on the CV as a measure for variation per source position for pixel 2, the DTW distances are leveraged. They can be used to describe the overall variation across sensor signals, for within-class (intra) in comparison with between-class (inter) distances. The distances are computed from all pairwise comparisons between untransformed time series of the respective category. The expectation for sensors with low signal-shape-based source distinction (e.g., a12) is low inter-class and intra-class distances (i.e., high similarity). Whereas sensors showing high distinction should record less similar curve shapes (e.g., b32), especially inter-class, therefore showing large distances. To compare all sensors, the mean and standard deviation for these two distance-based measures were calculated for pixel 2. The resulting mean DTW distances

are visualized in Figure 7.7, ranked from left to right, by the ratio of inter- to intra-class distance.

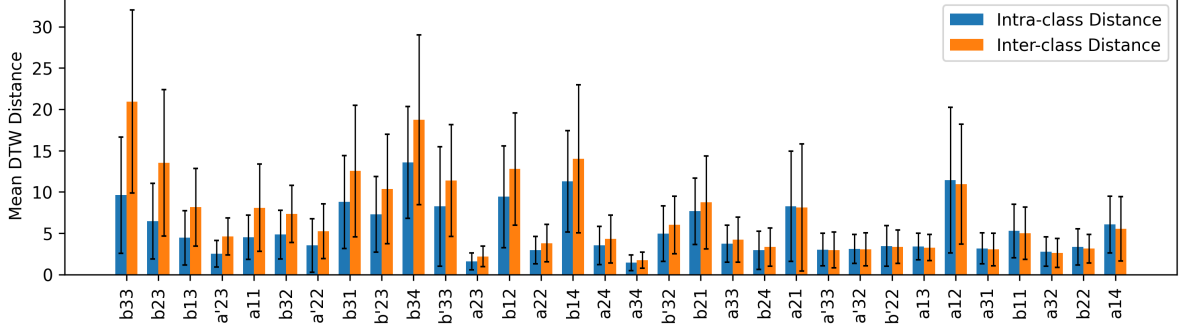


Figure 7.7: Bar plot representation of inter-class distances to intra-class distances, obtained as the mean of pairwise computed DTW distances of the respective category. Calculated from the untransformed time series measured with pixel 2, ranked by the ratio of inter-class to intra-class distances. Reprinted from [134].

The variability of the measurements with the sensors on the left of the figure is large across source positions, as they show higher between-class distances than within. This is the case for the sensor b23, previously identified as having high variability for position 2. For the sensors on the right side of the figure, in contrast, the intra-class distances are higher, suggesting the repeated measurements have high variability compared to measurements across source positions. Additionally, this visualization illustrates the high dependency on sensor position. Overall, mean DTW distances range from close to zero, to above 20. Variability appears to be higher for side b, especially for b33, b34, b14, while very low for a23, a34, and a32, which agrees with the identified differences in signal shape.

7.4 Sensor Placement

Using the two distance-based measures, a score can be introduced, describing the ability of a sensor to separate the classes:

$$\text{DTW Separability Score} = \frac{\text{mean inter-class DTW distance}}{\text{mean intra-class DTW distance}} \quad (7.2)$$

The score was calculated on pixel level first, then averaged to sensor level. If separability is achievable, the score will yield a single value above 1, by the intra-class distances being smaller than the inter-class distance values. From this score, sensor ranking was obtained for z-scores as well as the untransformed time series, as visualized in Figure 7.8. Most of the sensors, displayed in the bar plots in descending order, score above 1.0 and are therefore positioned well for the source distinction. Nevertheless, especially in the case of the untransformed data (Z-score False), many sensors are not informative regarding the source position.

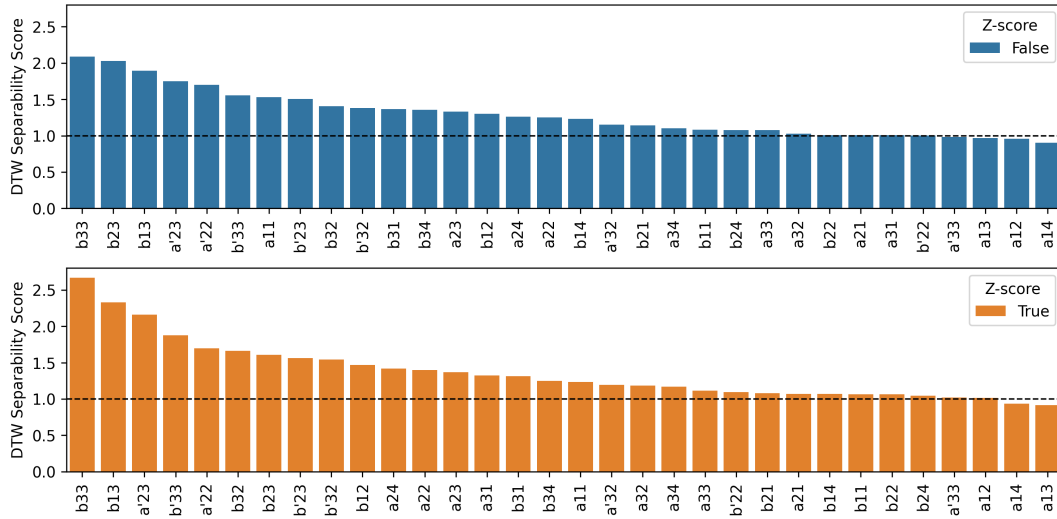


Figure 7.8: Bar plot representation of the DTW separability scores, obtained with the untransformed data in the upper panel and the z-scored data in the lower panel. A dotted line is displayed at a score of 1.0, indicating the decision border of separability. Reprinted from [134].

When comparing the individual sensors and their separability scores to the initial signal type categories in Section 7.1, the trends align. In the untransformed ranking, the sensors b33, b23 and b13 score the highest, however, the remaining sensors forming the T in Figure 7.1, b32 and b34 do not immediately follow. Instead a'23 and a'22 show higher separability scores, which was not visually clear, by untransformed sensor signals. The score provides a understandable measure, also incorporating pixels 1, 3, and 4, which could not be considered initially, because of the sheer amount of available data. The ranking from z-scored data slightly differs. For better overview, heatmap representations, visualizing the spatial position, are provided in Figure 7.9. Here, the similarity in trends, like the importance of b13, b23 and b33 on side b, or a22, a23 and a24 on side a are visible. Again, between a and a', as well as b and b', some local trends can be identified, underlining the positional importance and high variability of plume (across sources) in the light regions. For both cases of data processing, the side b shows higher scores, especially along $Z = 3$.

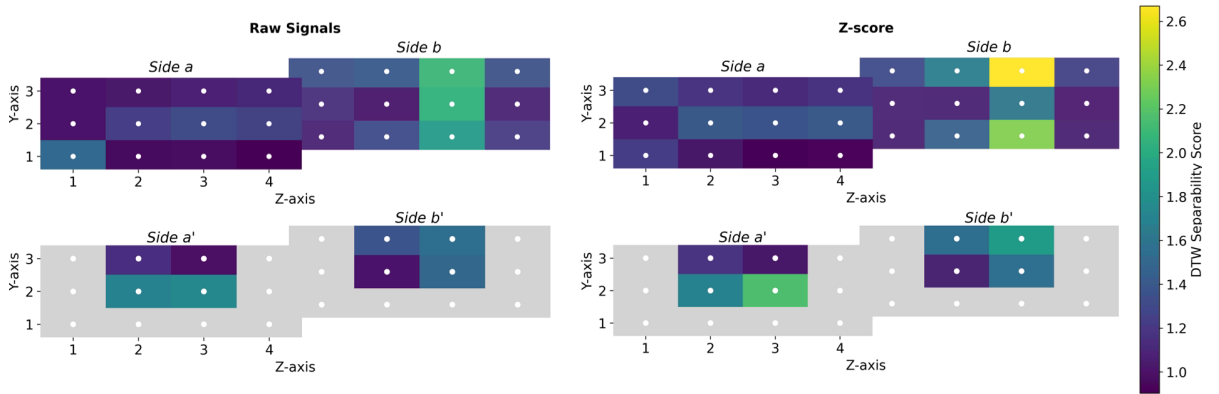


Figure 7.9: Heatmap representation of the DTW separability scores. The values are represented from dark to light. The raw signals are on the left and the z-scores displayed on the right side. Reprinted from [134].

An indication as to why the side b is more relevant, was obtained with an infrared image of the heat source, after completion of one heating run (Figure 7.10). Because the heat source relies on the unidirectional flow of the current through the wire, an asymmetrical heat propagation is difficult to balance. The left side of the furnace, notated with P1 and P3, faces side b in the ASTRA. The gradient of 5.7 K from P2 to P1 and 8.4 K from P4 to P3, naturally forces the plume towards the left.

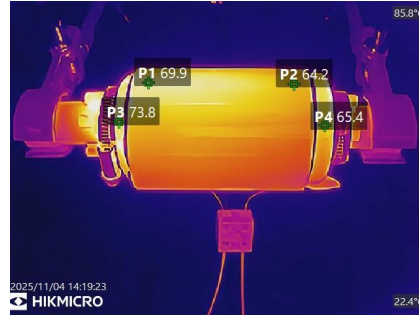


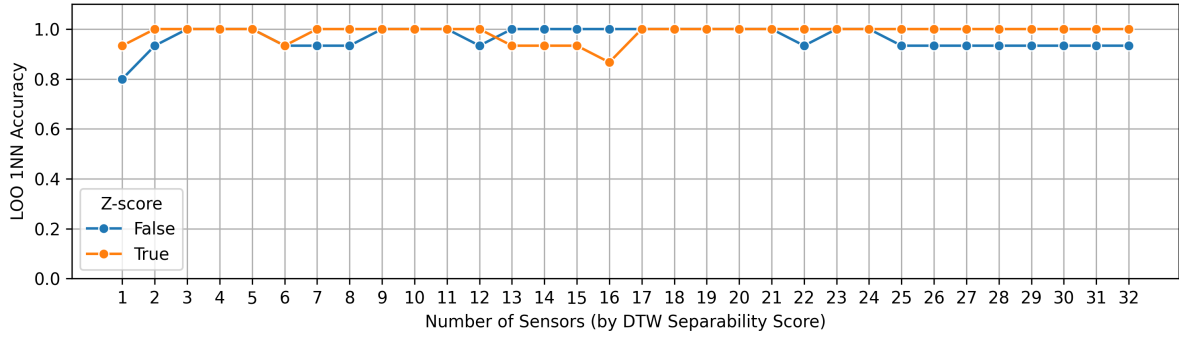
Figure 7.10: Infrared image obtained with the HIKMICRO Pocket 2 (Hangzhou Microimage Software Co., Ltd., China) at the end of a heating sequence. Reprinted from [134].

In summary, plume movement and consequently optimal sensor positioning in the experiment is governed by multiple factors, including the sample placement within the boat, the relative positioning of the boat and furnace, the degrees of freedom available to the plume within the test volume, and the characteristics of the heat source. These findings underscore the importance of experimental observation for gas plume tracking in the application of pre-ignition fire detection, particularly in complex environments.

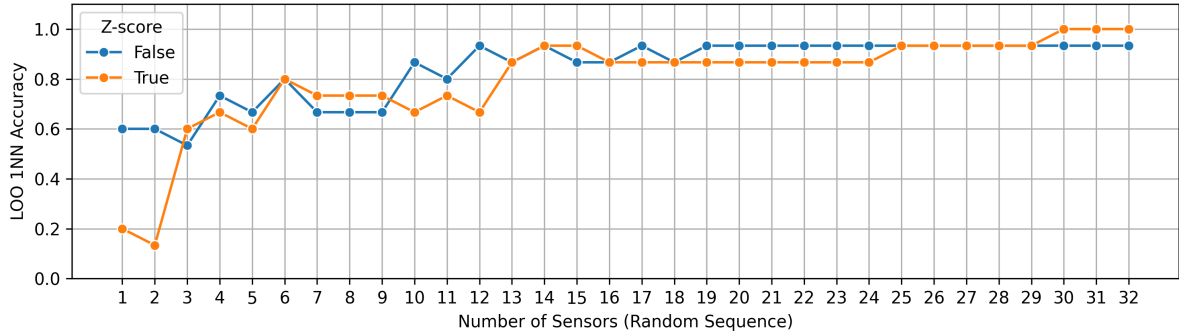
Reduction in Required Sensors

With the established DTW separability score a possible reduction of sensors is discussed in this section, achieved by starting with the highest scoring sensor in separability score and sequentially adding sensors to the DTW-k-NN pipeline. The first accuracy is therefore obtained using only one single sensor, the second by two sensors and so on. This results in 32 accuracy scores for each of the pre-processing methods, as visualized in Figure 7.11. Choosing the single best sensor, the accuracy with the sensor signals is at 80 %. Using the two best sensors, the score moves to 93 % and with three sensors to 100 %. When z-transforming the sensor signals, the k-NN scores 93 % with one, and 100 % with two sensors used. A lot of fluctuation on high values can be seen for both of the sequences for an increase in the numbers of sensors, stabilizing at 93 % for untransformed, and 100 % for transformed data.

A reduction in sensors is clearly possible, by consulting the DTW separability score. Conversely, randomly arranging the sensor sequence, 30 sensors (z-transformed) are necessary to reach 100 % accuracy, and 12 to reach 93 %. In the random sequence, the untransformed data never reaches 100 % accuracy.



(a) ranked by the DTW separability score



(b) ranked by a random sequence

Figure 7.11: Accuracies obtained from a selection of sensors, for the sensor signals with and without z-normalization. Reprinted from [134].

Generalization to Smaller Sample Masses

Three additional measurements were conducted with 100 mg, 104 mg, and 97 mg of sample mass to investigate the ability of the k-NN-framework to generalize to different masses. The smoothed sensor signals, recorded by pixel 2, are visualized in Figure 7.12, with the three measurements in bold colors and the previous 15 measurements in sheer colors. The signal magnitude overall is lower for the lower sample masses. Some similarities could be identified, like the larger amount of noise for position 2, recorded by b32, b33 and b34. However, from the selection of one fourth of available data, judging visual similarities using only one pixel, is insufficient. For a conclusive comparison, all of the initial measurements (15) were used for training and the three samples as separate test set. The DTW separability score was calculated to obtain a sensor ranking like in the previous sections.

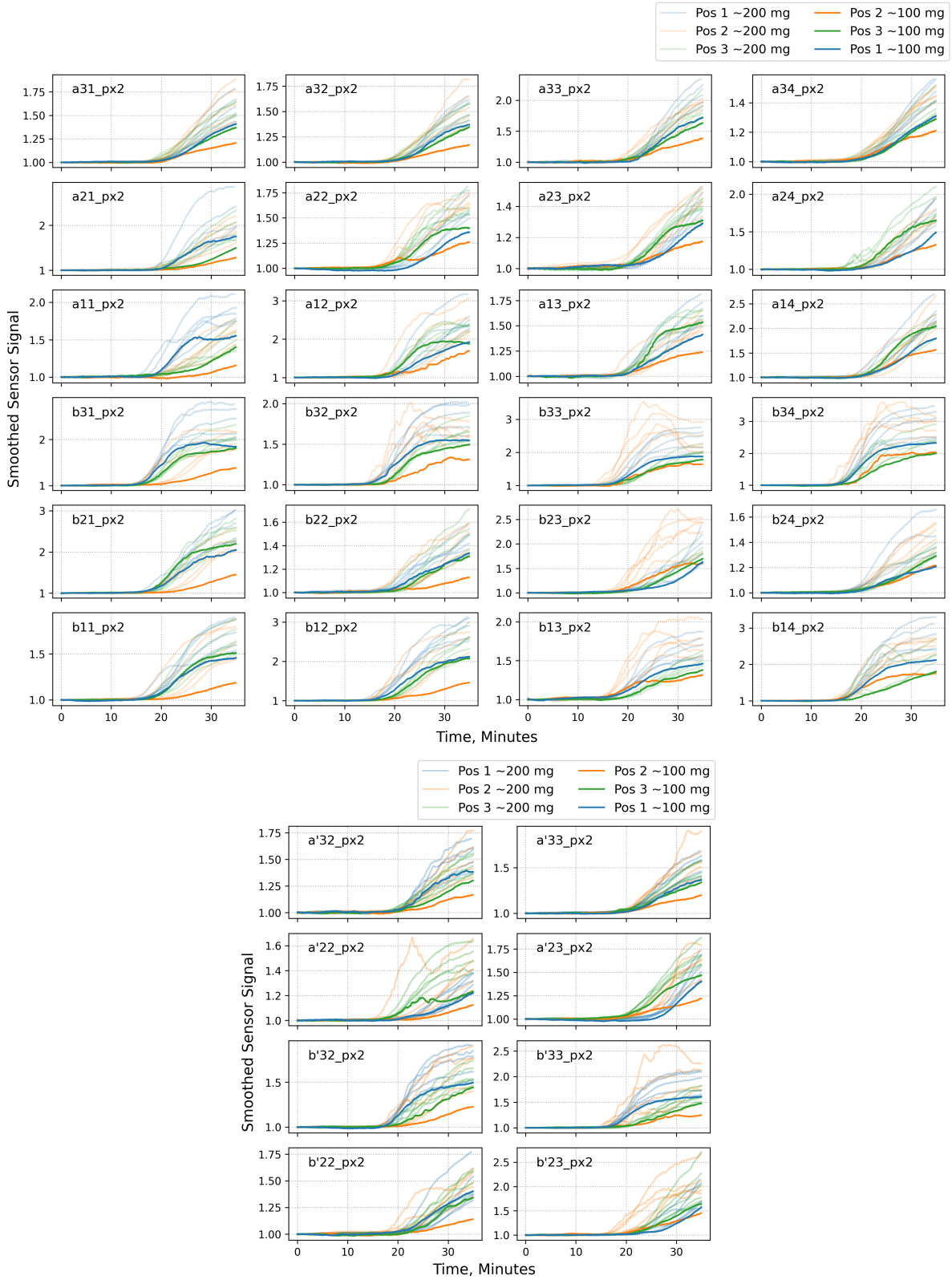


Figure 7.12: Sensor signals of sensors a, b, a', and b' pixel 2, smoothed with a rolling mean of five seconds, equal to five data points. The source location can be identified by color-coding, the approximate amount of sample by color intensity.

The mean accuracy, obtained from the three experiments as test data (one per source location), is overall higher for the z-transformed values, as visualized in Figure 7.13. This was to be expected, as the signal shape is less dependent on the sample concentration or mass, than the magnitude of the signal. For some combination of sensors, 100 % accuracy was reached using the z-scores. Nevertheless, using the entirety of SGP40 sensors employed in the ASTRA, yields 67 % accuracy for the transformed and only 33 % for the untransformed data. By changing the value of k to 3, 5, or 7, 100 % accuracy was reached, using all sensors after z-transformation* (see Figure 9.4 in the *Appendix*). The value of k is largely dependent on the dataset and often chosen in regard to the dataset size. A low k has high variance in comparison to larger values.

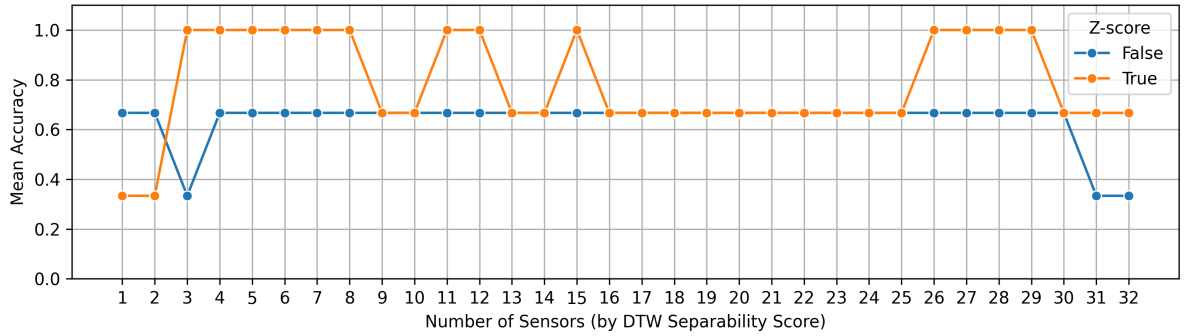


Figure 7.13: Accuracies obtained from a selection of sensors. Ranked by the DTW separability score for the sensor signals, with and without z-normalization, using only the three low-mass samples as test data.

As for the generalization to other modified polymers: at a fixed temperature, the recorded sensor signals reflect the plume trajectory and concentration differences within. For that reason, DTW should be applicable to any material, given significant and measurable outgassing at the selected temperature. Variations in concentration mainly influence the magnitude of signal over time (as exploited here), while variations in measured species might influence response dynamics.

This short digression delivers a rudimentary prospect on the ability to generalize with the proposed DTW-k-NN pipeline. The plume path is similar for changed masses, which makes z-transformation a necessary step to normalize the sensor signals to comparable shapes.

* As reference, with the initial set of 15 measurements using 200 mg per sample, the accuracy achieved with LOO was 1.00/0.8 for $k=3$; 0.8/0.6 for $k=5$; 0.8/0.6 for $k=7$ using z-scored/untransformed data of all sensors and pixels.

If changes should occur in background composition, for instance a change in relative humidity, the sensor response will be influenced. Slow and gradual changes can possibly be compensated for, as they mainly influence the signal magnitude. However, rapid changes during the measured overheating event need to be compensated for with additional sensors and more complex algorithms. With forced convection of pre-defined speed, like in [36], other evaluation approaches might be required. When placing the sensor in the air stream, localization could be achieved by comparing response times and locating the source as upstream of the sensors, with the fastest reaction or highest signal amplitude. The adequacy of training the sensors in forced convection is dependent on the application, but would give complementary information and is therefore planned for future experiments, as it was only reported in a limited number of flows and without repetitions in the scope of [149].

While this study is limited by the number of experiments, the number of sensors and pixels employed, provides significant amount of data. The initial objective to identifying feasibility and investigating the core methodology of the process, before further complicating with additional gases, was assessed and led to the insights necessary for further developments and conceptualization of experiments.

The coefficient of variation delivered insights in the plume movement and the gas source localization was successful. Based on the signal shapes, the DTW separability score has proven to be a powerful metric for the judgment on sensor placement. In combination, the evaluation methods led to an understanding of the possible plume trajectory and the importance of correct configuration-adjusted positioning of sensors. Similar evaluation methods could be applied to several safety-critical environments in order to optimize the configuration specific sensor distribution.

A comprehensive summary of the findings of this and the previous chapters, including the implications on future work, are supplied in the following.

8 Summary and Outlook

The feasibility of detection, temperature prediction, and source localization using commercial SMOX-based sensors was demonstrated for a selection of modified polymers used in space applications.

The ASTRA was constructed as a test vessel, containing the sensors and a heat source. From the brief assessment of the basic characteristics it was concluded that, according to the EL-USB-CO300 and Alc/C-100, sufficiently accurate dosing was achieved for the system to be used to inject labeled interfering gases. Liquid dosing, discussed on the example of ethanol, yielded less than half a ppm deviation as an average MAE for all of the concentrations tested. In case of carbon monoxide, representing the gas dosing functionality, a maximum MAE of 2.45 ppm was obtained. The concentration was represented as a function of time during different operational modes of the system. As a result, the time required to reach a concentration maximum was calculated for both analytes. The minimum duration required until the concentration decreases to zero during natural and forced decrease (by 'purging' the system) were reported for exemplary concentrations. Besides the use in continuation of this project, the ASTRA will be a valuable extension as a device for training, environmental studies and long-term stability experiments in gas sensor research.

The commercially available, digital SMOX-based sensor SGP40 was tested for its suitability to identify the temperature of heated PMMA, PDMS, Nomex and Kapton. First, a successful simple binary prediction conducted and the general suitability for PMMA identified. Afterwards, a larger dataset was obtained, to predict and distinguish the different polymers and their temperatures, based on the thermally induced outgassing. Ridge regression was compared to random forest and XGBoost, for sensors operated in constant and modulated operating temperature. The results quantify the large advantage of temperature modulated sensor operation. With the random forest regression MAEs in the range of 3 K to 10 K and MREs from 5 % to 15 % were obtained.

All materials show increasing outgassing with increasing temperature (100 °C to 150 °C to 200 °C), according to the chromatograms obtained using GC-MS. The lowest detector intensity was observed for the measurements on Kapton. However, at higher temperatures, not reachable using GC-MS due to instrumental limitations, Kapton outgassing is measurable with the sensor. The signal increase from PMMA was especially dominant for three species, out of which MMA occurred in significant abundance, already at 100 °C. The monomer is the most promising marker for this material, as it will occur across manufacturers and was measurable even in a diluted subsample of the headspace at 30 °C. The measurements on PDMS support the sensor readings, as they showed low abundance identified as siloxane-species, which the SGP40 is protected against with a specialized, undisclosed technology. Nomex is a promising material as it delivers many possible species that could be investigated further. The identification of species exiting the material not only support the findings and explain the shortcomings, but can also lead to the development of specialized SMOX-based sensors.

In the last chapter of reported results, the possibility of operating a sensor network, consisting of 32 SGP40 sensors within the volume of the ASTRA, is reported. 15 measurements, conducted with the source placement varying between three optional positions, led to 1920 time series for evaluation. The results allow for insights in the plume movement, determined in part by the experimental design and the therefore optimal sensor placement, using separability scores, derived from DTW distances. The sensor signals recorded the spatial and temporal gas plume trajectory, allowing for successful gas source localization, using DTW in combination with 1-nearest-neighbor classification. With the obtained dataset, the source location was predicted with an accuracy of 93 % or 100 % depending on data pre-processing. The number of sensors can even be reduced, while keeping that accuracy, using the aforementioned separability score as a guide for sensor selection. Aside from the successful localization, the most important finding is the identification of the information being contained in the signal shape, reflecting the trajectory of the gas plume. Z-transformation of the obtained sensor signals has proven to be essential for generalization to smaller samples masses and reduction of sensors.

Outlook

The reported studies enabled the continuation of this research in a follow-up project. Based on the experience gained, numerous studies are being planned or are already underway.

Together with our partners at the University of Bremen custom multi-pixel sensors, with application-tailored sensing layers deposited using Flame Spray Pyrolysis (FSP), are produced and tested. The advantage is that the sensing materials can be tuned specifically to the outgassing of the selected materials.

In order to identify the shortcomings of the SGP40 and find suitable sensors to add to the system, the ASTRA will be used for a better understanding: to distinguish the target gases from disturbances ambient air will be adjusted with gases found on the ISS, as reported in multiple articles about the measurements using the Analysing Interferometer for Ambient Air (ANITA) [136, 137]. The influences of common fluctuations and events in both, gradual and rapid changes of concentration, are of interest.

Naturally, the temperature modulation could be improved and tailored to the application. In the case of pre-ignition fire detection with time as the vital parameter, shortening the modulation will increase the time span for further steps after the identification of the hazard.

Studies on long term drift and its influence should be conducted in the application environment or a simulation of such. Schultealbert [167] discovered a characteristic for the state of intoxication from siloxanes, using sensors in temperature modulated operating mode, which can be used for self-compensation of the sensor signal. This concept might be applicable for sensor drift in general and is promising for drift-compensation in long term measurements.

Denser spaced source positions will help gain information on how to move from classification to regression, as the source position should be identified with three-dimensional coordinates, or localized in pre-defined zones.

To explain the movement and find the dead-end regions where the plume does not move, numerical simulations will be conducted, necessary especially for environments which do not allow for larger measurement campaigns. In many cases, restrictions apply, and certain requirements must be met in order to collect data in the target environments, as is the case, for example, with the International Space Station. In a cooperation with ZARM Technik AG in Bremen, the necessary steps are undertaken to come closer to

meeting the technical demands for a demonstrator, ready to be send to space.

In the meantime, stress tests on the sensors, measuring outgassing until complete material combustion, are planned in a fire-research chamber. Additionally, long-term tests of continuous monitoring in the Moon and Mars Base Analog (MaMBA) are planned to be executed by the project partners at the University of Bremen. The latter will be used to simulate an event in a furnished and partly occupied space, to train the system with interferences by humans.

While DTW was an optimal choice to test the feasibility of gas source location as conducted, the algorithm might be unsuited for on-line measurements or measurements in environments with (strong) forced convection. Besides the computational costs, any warping window could distort the time-resolution, which might be relevant for the localization in such a configuration. A small number of response-time measurements with different velocities of forced flow were conducted in the fire-research chamber [149]. However, further measurements are required for validation.

On that note, the amount of diverse data is often the greatest limitation for studies on sensor placement optimization, early fire detection, or smoke propagation due to safety constraints and laborious tests. As a more accessible addition to space habitats, the monitoring of data centers and cable shafts poses an interesting application for the sensor system in development. With the growing need for data-storage and at least since the fire in the data center OVH Cloud in March 2021 [170], the need for early warning systems, to prevent the spread of fire and allow for early action to mitigate damage, became obvious.

A strategy for the deployment of the demonstrator in development could be the integration in existing infrastructure. The use of such multi-modal systems can improve the current level of fire-safety by detecting early signs of fires (pre-ignition) and validating them through existing sensors and infrastructure.

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Acronyms

AGS amperometric gas sensor

ANITA Analysing Interferometer for Ambient Air

ASTRA Ambient-air Sensor Training and Research Apparatus

AUC area under the curve

CSG chemical sensor grid

CV coefficient of variation

DTW dynamic time warping

ECLSS Environmental Control and Life Support Systems

ESG single-pane safety glass - Einscheiben-Sicherheitsglas

ETFE polyethylene tetrafluoroethylene

FN false negative

FP false positive

FTIR Fourier transform infrared spectroscopy

GC-MS gas chromatography-mass spectrometry

GMS gas mixing system

GSL gas source localization

GUI graphical user interface

ISS International Space Station

k-NN k-nearest neighbors

LDA linear discriminant analysis

LEO Low Earth Orbit

LOO leave-one-out

MAE mean absolute error

MAK Maximale Arbeitsplatzkonzentration - maximum workplace concentration

MFC mass flow controller

MMA methyl methacrylate

MRE mean relative error

NASA National Aeronautics and Space Administration

NIST National Institute of Standards and Technology

PCA principal component analysis

PDMS poly(dimethylsiloxane)

PEEK polyether ether ketone

PFA perfluoroalkoxy alkane

PMMA poly(methyl methacrylate)

PTFE poly(tetrafluoroethylene)

PVC polyvinyl chloride

RE relative error

RMP Reflow Master Pro

RMSE root mean squared error

ROI region of interest

SAME Smoke Aerosol Measurement Experiment

SMAC Spacecraft Maximum Allowable Concentrations

SMOX semiconducting metal oxide

SNR signal-to-noise ratio

TGA-MS thermogravimetric analysis-mass spectrometry

TH threshold

TMM temperature modulation mode

TN true negative

TP true positive

VOC volatile organic compound

XGBoost eXtreme Gradient Boosting

Publications

Articles in Peer-Reviewed Journals

- L. Schynowski, F. Meyer, U. Weimar, N. Bârsan, “Exploring Pre-Ignition Source Localization Using a 3D Network of Semiconducting Metal Oxide Gas Sensors”, *Sensors and Actuators B: Chemical* **2026**, 467, 140442.
- C. Gienger, L. Schynowski, J. Schaefer, C. Schrenk, A. Schnepf, “New Intermetalloid Ge₉-Clusters with Copper and Gold: Filling Vacancies in the Cluster Chemistry of [Ge₉(Hyp)₃][−] (Hyp = Si(SiMe₃)₃)“, *European Journal of Inorganic Chemistry* **2023**, 26, e202200738.

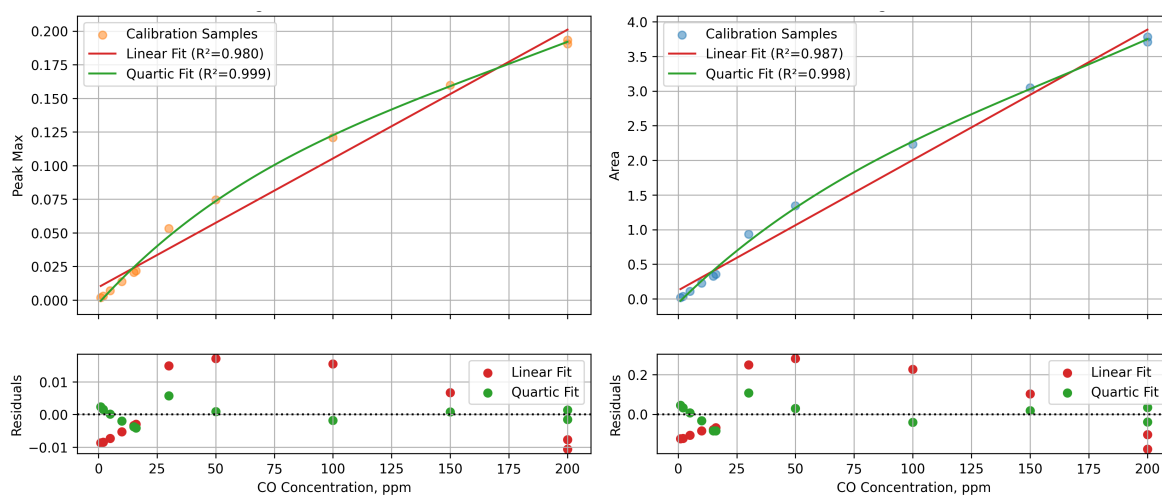
Peer-Reviewed Conference Papers

- L. Schynowski, A. Kobald, H. Solomon, F. Meyer, M. Schalk, L. Mädler, U. Weimar, N. Bârsan, “Towards Application of SMOX Sensors for a Pre-Ignition Fire Detection System“, **2025**, ICES-2025-316.
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- L. Schynowski, A. Kobald, U. Weimar, N. Bârsan, M. Schalk, F. Meyer, C. Eigenbrod, L. Mädler in 17th Dresdner Sensor-Symposium, **2024**, pp. 43–46.

Appendix



(a) peak maximum against CO concentration

(b) AUC against CO concentration

Figure 9.1: Linear and quartic fit applied to the calibration data with corresponding residuals in the bottom panels.

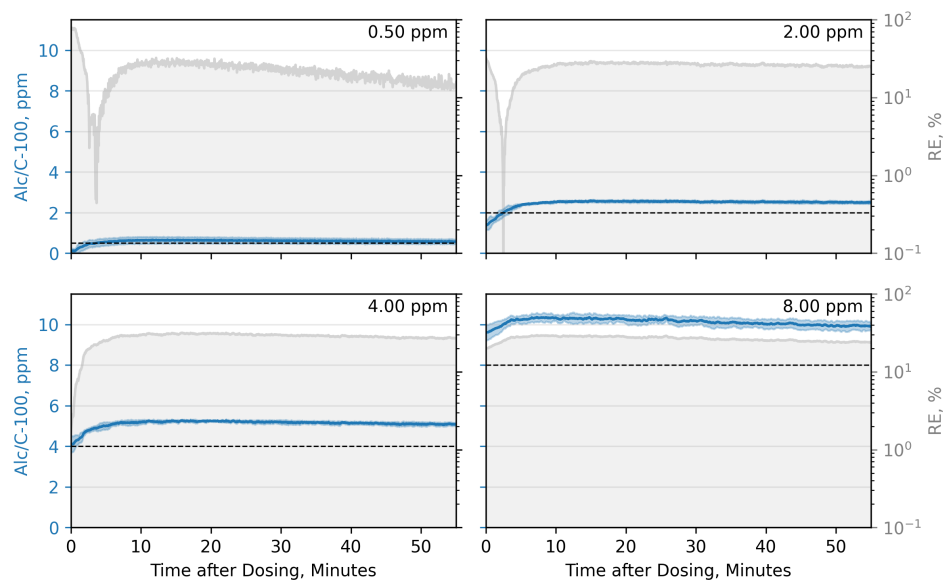


Figure 9.2: Mean concentration and standard deviation against the time after ethanol gas dosing was stopped. On the secondary y-axis, the absolute of the corresponding relative error is displayed. The mean predicted concentration by the software of the ASTRA is displayed in the upper right per panel and as a horizontal dashed line.

Table 9.1: Errors obtained for concentrations of EtOH, supplied by the gas dosing mechanism of the ASTRA and using Alc/C-100.

Calculated Concentration, ppm	Concentration of Gas Added, ppm	Gas Added	RE, %	Error, ppm
15.06	-	-	-11.58	-1.56
15.03	-	-	6.05	0.97
15.03	-	-	6.07	0.97
15.07	1.01	syn. air	8.69	1.43
15.07	2.51	syn. air	11.33	1.93
15.04	5.01	syn. air	8.85	1.46
30.06	-	-	6.06	1.94
30.07	-	-	6.02	1.93
30.04	-	-	6.13	1.96
30.05	1.01	syn. air	6.09	1.95
30.05	2.51	syn. air	6.08	1.95
30.05	5.00	syn. air	6.08	1.95
15.03	-	-	-3.67	-0.53
15.06	-	-	11.43	1.94
15.05	-	-	8.79	1.45
15.06	1.01	EtOH	11.39	1.94
15.03	2.51	EtOH	11.60	1.97
15.03	5.00	EtOH	11.59	1.97
30.04	-	-	8.96	2.96
30.05	-	-	8.95	2.95
30.05	-	-	7.54	2.45
30.06	1.00	EtOH	6.05	1.94
30.03	2.51	EtOH	6.16	1.97
30.08	5.00	EtOH	7.46	2.42

Table 9.2: Hyperparameters of best performing models, selected on the basis of the RMSE. The data was recorded with the sensor in constant operation, using the single-material dataset.

Model	Hyperparameter	PMMA	PDMS	Nomex	Kapton
Ridge Regression	α	0.5	1.0	1.0	1.0
Random Forest	n_estimators	300	300	100	300
	max_depth	None	10	None	None
	min_samples_split	2	2	2	2
XGBoost	n_estimators	200	200	200	200
	max_depth	3	5	5	3
	learning_rate	0.1	0.05	0.05	0.1
	subsample	1.0	1.0	1.0	1.0
	colsample_bytree	0.8	0.8	1.0	1.0

Table 9.3: Hyperparameters of best performing models, selected on the basis of the RMSE. The data was recorded with the sensor in constant operation, using the multi-material dataset.

Model	Hyperparameter	Combined Materials
Ridge Regression	α	1.0
Random Forest	n_estimators	300
	max_depth	None
	min_samples_split	2
XGBoost	n_estimators	200
	max_depth	5
	learning_rate	0.05
	subsample	0.8
	colsample_bytree	0.8

Table 9.4: Hyperparameters of best performing models, selected on the basis of the RMSE. The data was recorded with the sensor in TMM 2, using the single-material dataset.

Model	Hyperparameter	PMMA	PDMS	Nomex	Kapton
Ridge Regression	α	1.0	0.5	1.0	0.1
Random Forest	n_estimators	200	300	300	100
	max_depth	None	None	None	10
	min_samples_split	2	2	2	2
XGBoost	n_estimators	200	200	200	200
	max_depth	3	3	5	3
	learning_rate	0.1	0.1	0.1	0.1
	subsample	0.8	0.8	1.0	1.0
	colsample_bytree	1.0	1.0	0.8	1.0

Table 9.5: Hyperparameters of best performing models, selected on the basis of the RMSE. The data was recorded with the sensor in TMM 2, using the multi-material dataset.

Model	Hyperparameter	Combined Materials
Ridge Regression	α	0.1
Random Forest	n_estimators	200
	max_depth	None
	min_samples_split	2
XGBoost	n_estimators	200
	max_depth	5
	learning_rate	0.1
	subsample	0.8
	colsample_bytree	0.8

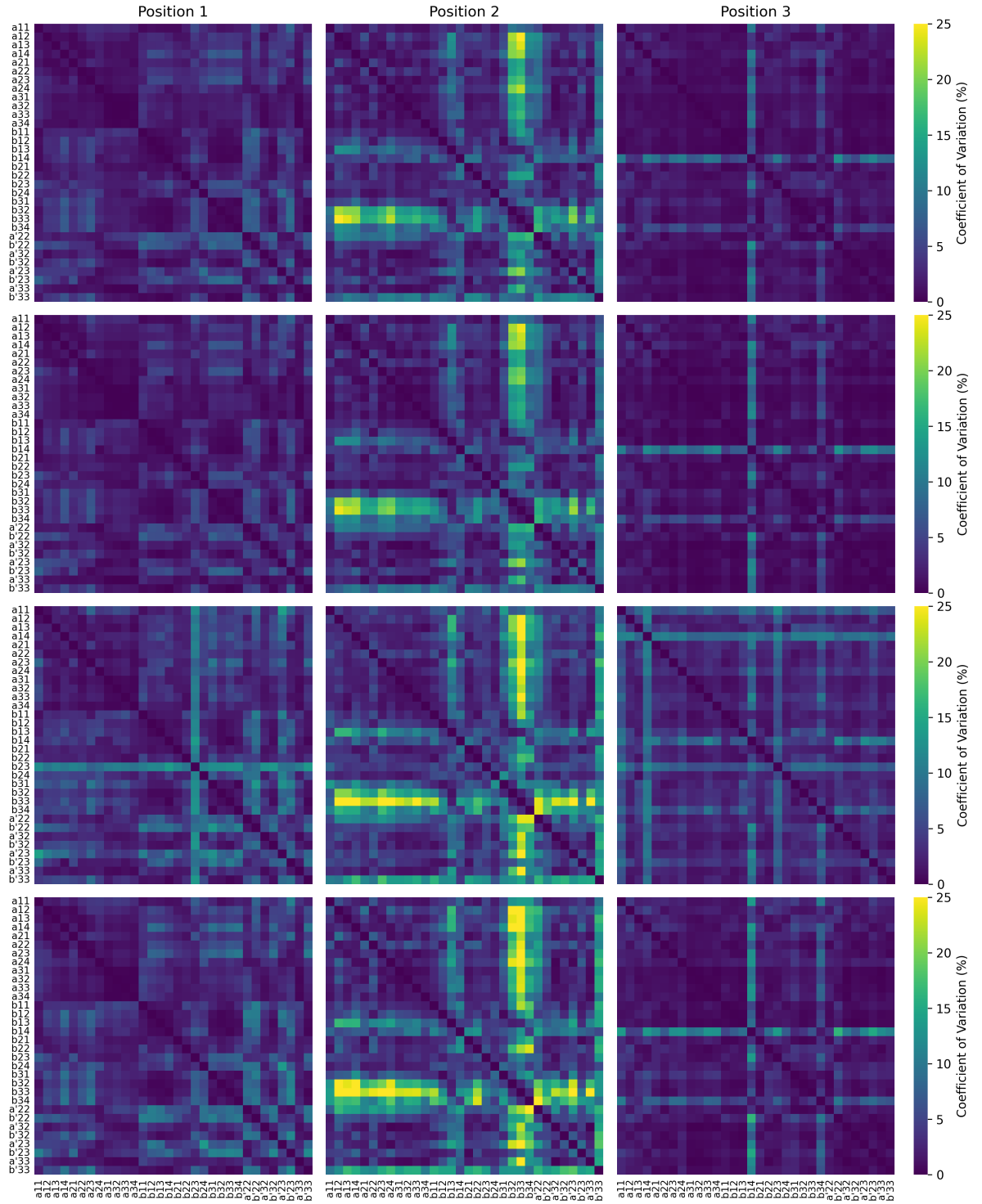


Figure 9.3: Matrices displaying the coefficient of variation for all three source positions. From top row to bottom: the results for pixel 1, pixel 2, pixel 3, and pixel 4. In part reprinted from [134].

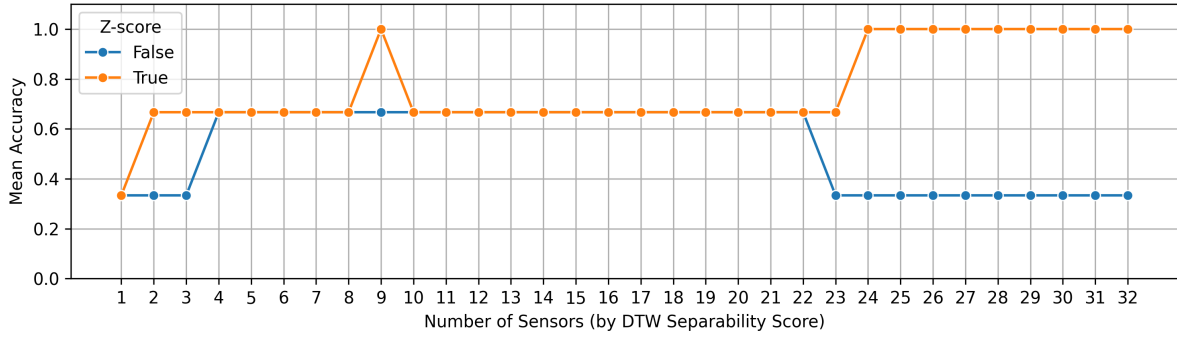
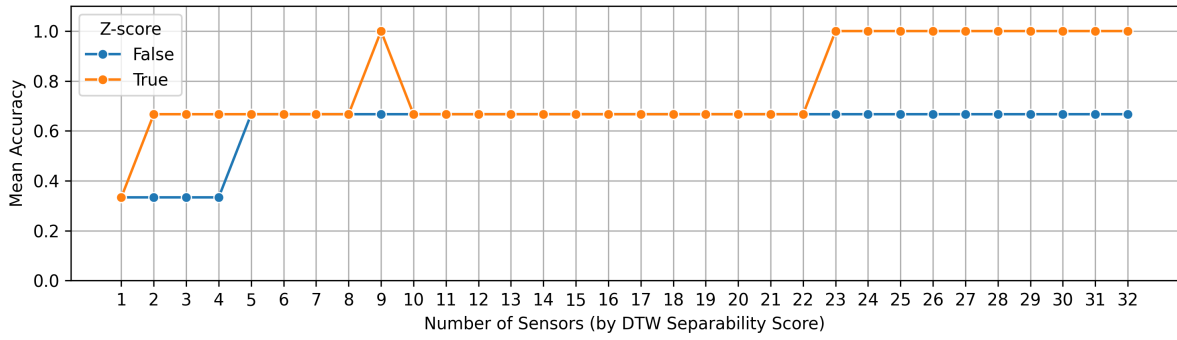
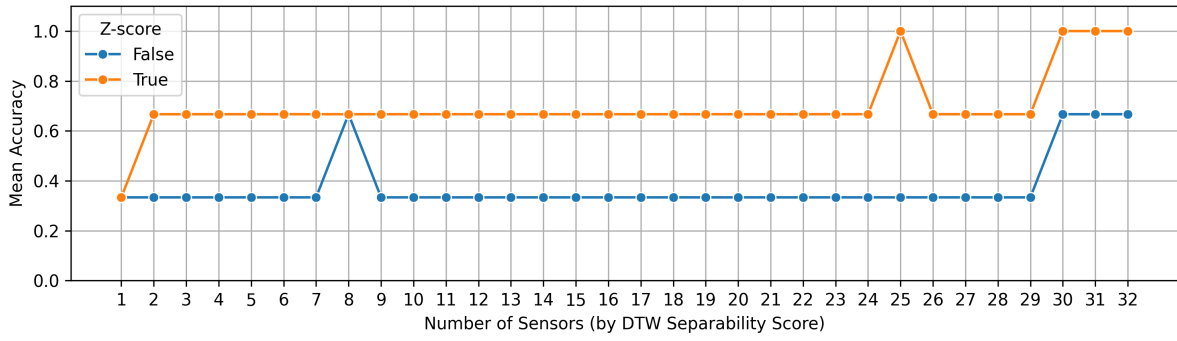
(a) $k = 3$ (b) $k = 5$ (c) $k = 7$

Figure 9.4: Accuracies obtained from a selection of sensors for different values of k . Ranked by the DTW separability score for the sensor signals with and without z-normalization, using only the three low-mass samples as test data.