

Consumption of Atmospheric Oxygen as Ageing Indicator of HTPB-based Solid Rocket Propellants

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Abstract

Changes in material parameters of solid rocket propellants (SRP), which have influence on its in-service time are considered as ageing. One main reason for ageing is the effect of atmospheric oxygen. In general, oxygen causes additional cross-links within the hydroxyl-terminated polybutadiene (HTPB) binder network, which increase Youngs-modulus. During this process, atmospheric oxygen is consumed by adsorption, diffusion, dissolution and chemical reaction. The oxygen concentration in the atmosphere around the SRP sample material is followed with Raman spectroscopy and fluorescence-quenching of an oxygen sensitive fluorescence sensor, whereby the latter showed better results. Measurements were performed in a closed vessel and in a sealed model rocket motor in a temperature range from 30 °C to 90 °C. Appropriate models were applied to describe the reaction kinetics, which underlies the observed decrease of atmospheric oxygen concentration.

Keywords: composite rocket propellant; oxygen consumption; fluorescence-quenching method; solid rocket motor; kinetics; Raman-spectroscopy

1 Motivation

Properties of the SRP grain often define the in-service time (IST) of a SRM. Such properties change due to various effects, like oxygen attack, plasticizer migration or humidity attack. These changes are, if they reduce IST, referred to as ageing. To avoid ageing, after manufacturing then SRM is usually evacuated, flooded with inert gases like nitrogen and finally sealed against environmental conditions. But often, after a certain time of bunker storage, SRMs were found just not to be tight. Within the scope of the authors PhD activities in Fraunhofer ICT, this work concentrates on the evaluation of the oxygen consumption within an experimental SRM. Parts of this PhD-work have been reported in the past and should be

seen in connection with this part, see [1-4].

Mostly the ageing reactions accelerate with increasing temperatures. It is therefore of fundamental importance to know the kinetic of the involved processes. Methods for effectively studying the time-temperature relationship of the impact of ageing on mechanical parameters, obtained for example by DMA experiments are already described [5]. The main mechanism, oxidative attack, is subject of several studies. A correlation between oxygen consumption and the change of mechanical parameters was found for PU-foams using respirometer, ultrasensitive oxygen consumption (UOC, using GC) and mechanical compression measurements [6]. The activation energy in a temperature range from 50-140 °C was determined to 87 kJ/mol, indicating a change in the mechanism for temperatures lower than 50 °C. Former measurements of the oxygen consumption of HTPB/AP/Al propellants, ranging from 25-125 °C showed a switch of the mechanism, which could be described well by low activation energies at lower temperature levels [7]. An overview about performed experiments, which indicate a switch of the reaction mechanism at a certain temperature, is given by [8]. For assessing the stability of NC-based propellants STANAG 4582 suggests a switching temperature of 60 °C, which was experimentally determined by stabilizer consumption, NMR and molar mass decrease of NC, resulting in two activation energies of 80 and 120 kJ/mol [9].

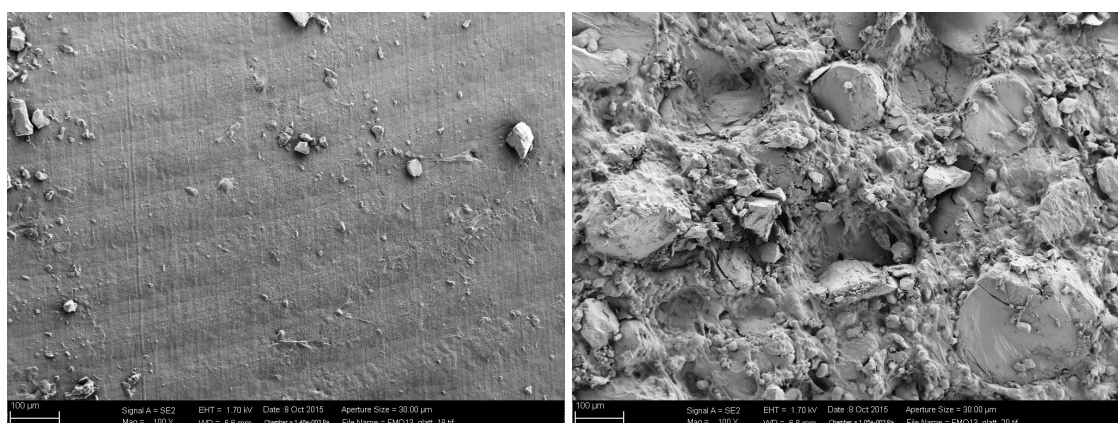


Fig. 1: SEM images of SRP FMO13. Left: surface generated by moulding tool. The crumbs are contaminations from uncontrolled storage; crumbs on smooth surfaces caused by moulding tools are usually defined as trash. With same preparation and SEM-parameters: surface after cutting of the same SRP.

A new method of measuring oxygen in gas-phase is fluorescence-quenching of a fluoromer substance caused by oxygen. It is very sensitive, especially in regions of low oxygen concentrations and is available on the commercial market. Therefore, the consumption of atmospheric oxygen within a sealed SRM was analysed in a temperature range from 30 °C up to 90 °C. For validation, a reference experiment was designed, using Raman scattering in the gas-phase.

The two experiments have one significant difference. Sample material used in the reference cell experiment (the setup 'outside' the SRM is referred to as reference cell) was cut into small pieces. The surface of this material looks completely different than the smooth propellant surfaces generated by moulding tools, see Fig. 1. It is very difficult to assess and to study the impact of the surface structure to the oxygen consumption behaviour. Just to mention: the measurement of the so-called BET surface did not work for this kind of SRP. Strictly seen, the mechanism of oxygen consumption within a rocket motor cannot be studied with a reference experiment using cut material because of this difference in surface smoothness. Inside of the motor smooth surfaces were found, see Fig. 2 and compare to Fig. 1. To achieve a representative external experiment, a special moulding tool for curing is necessary to obtain propellant sample material in the shape of small cubes or cylinders, which

are covered from all sides by a thin layer of binder. However, even then the material produced in such way may be not comparative to bigger blocks of SRP because of geometrical reasons.

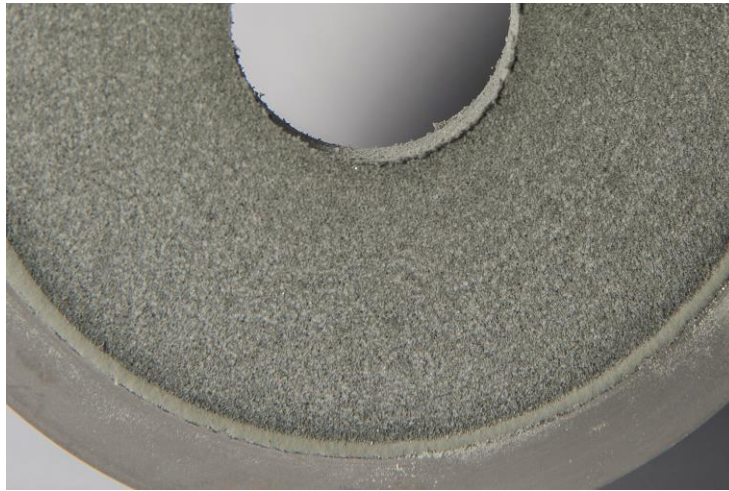


Fig. 2: Ring-segment, cut from the investigated model SRM. Compare to Fig. 1; bore surface is smooth, because just binder material is exposed to the side of the mould surface, here is was the mandrel coated with teflon.

At least as long as no correlation between the behaviour of cut sample material and bulk material is found (or believable) it seems to be inevitable to assess the oxygen consumption reaction directly on a motor-scale experiment.

2 Experimental Setup

2.1 Measurement in Solid Rocket Motor (SRM)

One of four SRM, formerly intended to be used to measure the influence of ageing assessing the bondline-stresses, see also 0, was used for the oxygen consumption experiment. The Fig. 3 shows details of the SRM. The motor type is case bonded solid rocket motor with cylindrical inner bore. Sealing of the SRM is achieved by two O-rings made of EPDM as well as one washer (on the right screw, see Fig. 3), coated with polymeric sealing material. Within the experimental time domain the diffusion of molecular oxygen from outside to inside through the polymeric sealing, and also their potential to consume molecular oxygen from the inner atmosphere can be neglected.

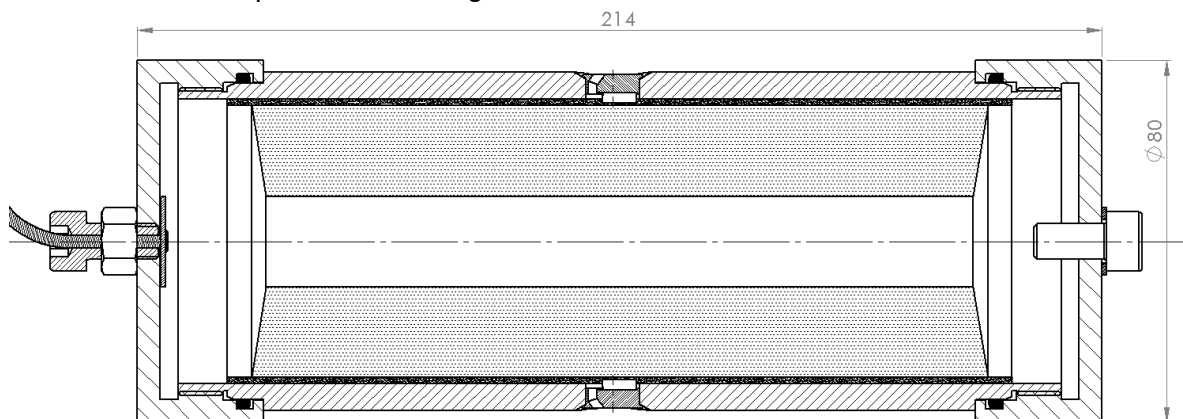


Fig. 3: Sketch of the used SRM. Inner SRP surface is 127 cm², air volume is 191.2 cm³.

The propellant and insulation used within this motor were manufactured at Fraunhofer ICT; the compositions are given in Table 1. The insulation layer is not just representing a thermal insulation, but here applied as layer for improving the adhesive contact to the case of the SRM made of stainless steel. See also Fig. 2 for aa view on the bond-line setup. Considerable analysis of the propellant FMO13 and also the whole family of propellants referred to with the term FMO was done prior to this experiment. It is known, especially for FMO13, that the sensitivity of mechanical properties, like Youngs-modulus (obtained by tensile test) or loss-factor (obtained by DMA) is smaller than for other propellants made by ICT. This may be a consequence of the antioxidant content within the used HTPB and not using a burning catalyst for AP.

Table 1: Composition of the composite solid rocket propellant and the insulation used in the four model motors.

Propellant FMO13		Insulation ICT22	
substance	mass-%	substance	mass-%
HTPB R45M	8.86	HTPB R45HTLO	53.1
IPDI	0.69	1,2,4 Butantriol	0.39
TPB	0.02	IPDI	6.1
DOA	4.1	Irganox 565	0.2
HX878	0.15	TiO ₂	1.9
Irganox 565	0.2	SiC	4.5
AP 45 μ m	12	Tegosil SiO ₂	33.8
AP 200 μ m	56	D22	3 drops
Al 18 μ m	18		

After casting, curing for nearly 7 days at 58 °C and mandrel extraction, one of the four SRM was stored under ambient conditions at a temperature of approx. 23 °C for nearly 10 months. The motor was sealed but not flooded with inert gas - so oxygen from the manufacturing could already migrate into the SRP grain. After this time, the SRM was equipped with an oxygen sensitive detector element on the inside of a glass window sealing, which can be sampled from the outside by optical way via a glass fibre. The setup is shown in Fig. 4 and in detail in Fig. 5. The motor was tested for tightness by applying vacuum through the opening on the right side, see Fig. 3.

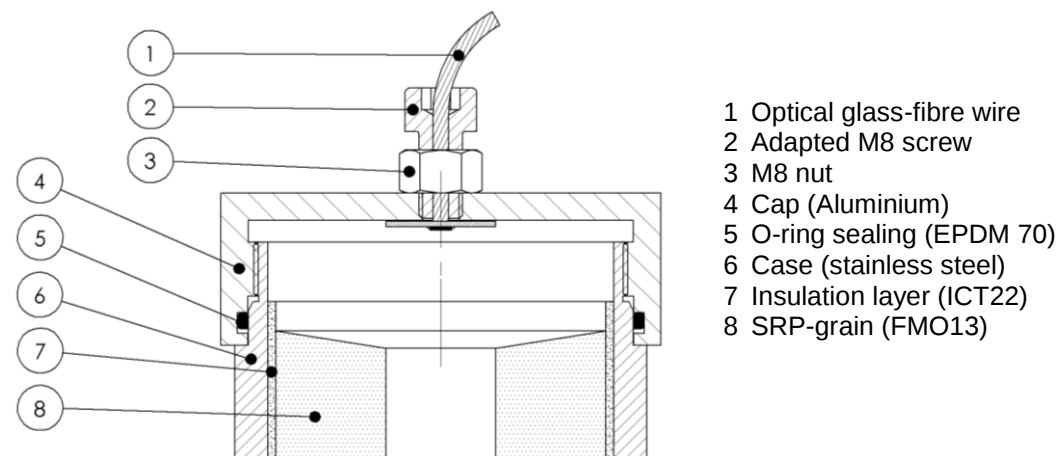


Fig. 4: Internal view of the SRM with optical oxygen sensor, see also Fig. 5.

This experiment with the SRM was planned to be a pre-trial and therefore no effort was made to fill the setup with technical air. The experiment was done with ambient air of an

oxygen concentration of typically 20.95 vol-%. With regard to inaccuracy at least the value of oxygen concentration is known better than for synthetic gas mixtures.

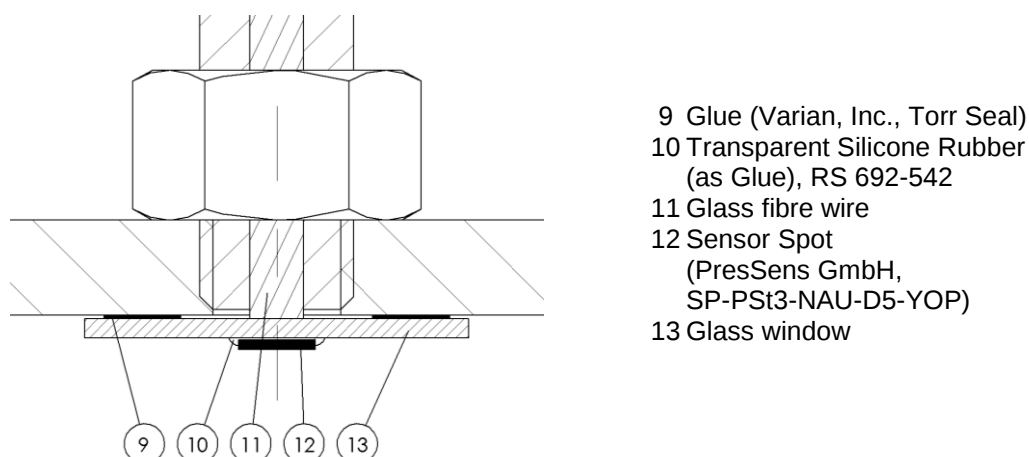


Fig. 5: Arrangement of the sensor spot in detail. Inner parts point downwards.

2.2 Reference measurement in closed vessel

In addition to the measurement of the oxygen consumption inside of the SRM an experimental reference cell was designed, in which the gas composition can be analysed using Raman-spectroscopy and fluorescence-quenching at the same time, see Fig. 6. The instrument can be used up to temperatures of 80 °C and was manufactured by the ICT workshop.

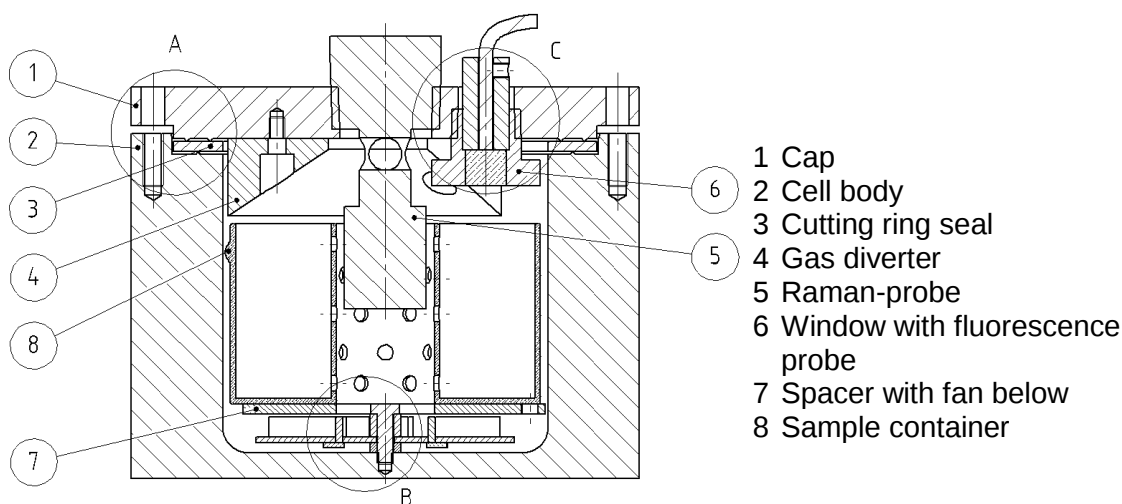


Fig. 6: Sketch of the reference cell. Part 3 made of silver-plated copper ring.

Perfect gas tight sealing is absolutely important for the experiment, so all passages through the housing, where the author had influence on, were designed to ensure tightness. The main seal of the cap is realised by a cutting ring seal. The sealing material is made of copper, coated with silver because of its smaller reactivity. One tube acting as gas supply is welded to the cap (not shown in Fig. 6). Two further passages are necessary: a window for the fluorescence-quenching equipment and a bore for the Raman probe. Both holes are self-sealing with a NPT-kind thread. These threads are sealed additionally with PTFE-tape. After assembly the threads are finally sealed from the outside with a highly filled paste called Torr Seal. Further design criteria were a minimum inner gas volume to improve sensitivity, a fan

used for gas circulation driven by magnet stirrer from outside and the minimum use of polymeric materials inside the experimental chamber.

Sample material, preferably cut into small cubes for larger surface area (see Fig. 7) is placed in a container made of glass. Small bores in the sample container ensure best flowing of the gas through the sample material. The fan on the bottom of the reference cell works as radial compressor with the low-pressure intake in-line with the channel of the sample container, providing an air flow upwards in between the inner wall of the cell body to the diverter, which deflects the stream into direction of the Raman probe and back down to the fan.



Fig. 7: View into the reference cell with material of FMO13 (left), Sensor mountings and cutting ring on the cap (right). SRP surface is $430 \pm 50 \text{ cm}^2$, air volume is 110 cm^3 .

The Raman equipment used is from company Kaiser Optical Systems, Inc., USA. As probe the AirHead™ gas-phase Raman probe was used in corporation with the RamanRxn2™ multichannel analyser. The reference cell was placed in a standard laboratory oven, connected via glass fibres to the analysers, see Fig. 8. Further, a data logger with thermocouple was used to track the temperature close to the reference cell inside of the oven.

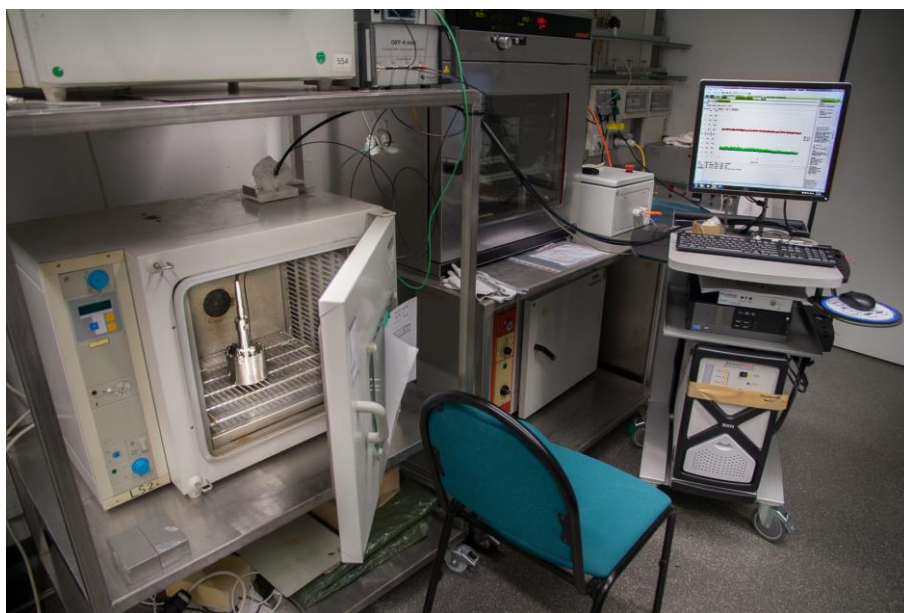


Fig. 8: Reference cell in oven (left) and Raman analyser with PC on the right. Above the oven with reference cell, the fluorescence quenching analyser is placed on the right

All Raman measurements were done with a porous filter around the probe part, see Fig. 7, right picture. The wavelength of the laser source was 532 nm. The sampling interval was set

to 15 min, integration time was found to be good with 1 min. The wavenumber resolution of the system was set to 1 cm^{-1} . For the experiments, two probes were available. One (probe 2, used for the experiment, RFQ-2) was disassembled once (removing of the porous filter element) during a technical introduction by the manufacturer. Maybe some inaccuracy caused misaligning of the focus of the probe, which may be the reason for the reduction of the peak intensity of (at least) factor 10, compare Fig. 15 and Fig. 16. Despite this observation the measurement was continued, because of the high preparation and assembly effort of the experimental setup. The impact on the scattering of the signal of interest, in this case the relation of oxygen to nitrogen peak surface, is low.

3 Theory of oxygen induced fluorescence-quenching

The effect of quenching of fluorescence of a fluoromer by oxygen is known since a long time [10]. Current and expired patents are available, see [12]. An example of the active site of such a fluoromer is shown in **Fehler! Verweisquelle konnte nicht gefunden werden..**

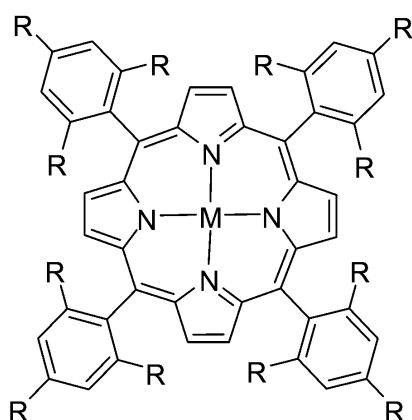


Fig. 9: Example of an oxygen sensitive fluoromer (M stands for Pt): Platinum tetrakis (2,4,6-triethylphenyl) porphyrin.

The fluorescence is induced by an external light source, here caused by excitation with visible light from a LED. Some materials like polycyclic aromatic hydrocarbons, transition metal complexes of Ru(II), Os(II) and Rh(II) or phosphorescent porphyrins containing Pt(II) for example as central atom, often called as luminophores, show fluorescence emission behaviour, which is dependent of the oxygen concentration of the environmental fluid (liquid or gaseous). In these materials, molecular oxygen quenches the fluorescence intensity. The used sensor system of type *OXY-4 mini* from company PreSens GmbH, Germany, measures the fluorescence intensity and decay time. The fluorescence behaviour is described by the Stern-Volmer equations, see Eq. (1).

$$\frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + K_{SV} \cdot [O_2] \quad (1)$$

I	Fluorescence intensity
τ	decay time
K_{SV}	Stern-Volmer constant
$[O_2]$	quencher concentration (here oxygen)
Index 0	refers to the state in absence of the quencher

When exciting the luminophore with sinusoidally modulated light intensity, a time delay between the excitation and the emitted (response) signal is caused. This relation is expressed

in Eq. (2), which suggests measuring the phase shift, which is less sensitive to aligning or ambient light irritations [13].

$$\tan \varphi = 2\pi \cdot f \cdot \tau \quad (2)$$

φ phase shift
 f modulation frequency of excitation source

Models, which are more accurate for the used sensor system than the original Stern-Volmer equation, are empirically developed. The suggested modification of the Stern-Volmer equation is given by Eq. (3).

$$\frac{\tan \varphi_0}{\tan \varphi} = \left(\frac{f_1}{1 + K_{SV} \cdot [O_2]} + \frac{1 - f_1}{1 + \frac{1}{x} \cdot K_{SV} \cdot [O_2]} \right)^{-1} \quad (3)$$

f_1, x empirical factors

The referred equations contain no temperature dependence of the fluorescence behaviour. A lot of research was done by Stehning and Holst with regard to this subject, see [14]. They show, that τ_0 , f_1 and K_{SV} are temperature dependent in a linear way and suggested a model, which incorporate these effects. The sensor system delivered by PreSens is calibrated with such a kind of model.

The fluoromer used by PreSens GmbH is propriety of the company and not exactly communicated. It is applied in small disks; means embedded in a silicon matrix. The whole sensor is also called optrode. It is used on a glass window; the optrode is in contact with atmosphere to be analysed. The probing is made from the other side of the window by thin optical glass fibres. This experimental setup was calibrated at room temperature for oxygen concentrations of 0, 20.95, 20 and 50 vol-%. The latter concentrations were applied by technical air and a mixture of oxygen and carbon dioxide.

4 Data Evaluation

For both experimental set-ups, the data treatment of the fluorescence-quenching measurement is the same; it is described in chapter 4.1. Data evaluation of the Raman experiment will be described only in short in chapter 4.2, because it is established technology.

4.1 Oxygen consumption inside SRM

The experiment was carried out at Fraunhofer ICT in a standard universal oven type Memmert UFE500 in a cellar room with controlled room temperature, see Fig. 10. The latter is important for the accuracy of the PID controlled temperature constancy. The room is dark and rarely frequented by just a small group of ICT personnel, to minimize external interfere to the measurements. Oven temperature was checked with a calibrated reference thermometer for about the second half of the experimental time, also shown in Fig. 10; a larger amount of oil ensures higher heat capacity and therefore smaller temperature fluctuations, seen by the reference thermometer.

The temperature compensated overall measurement data are shown in Fig. 11. Factor f_1 , see Eq. (3), was slightly varied (0.808 to 0.91) from the datasheet value of the manufacturer to obtain (1) a smooth course of the concentration and (2) a start concentration of approx. 100 %

air saturation (means 20.95 vol-% of oxygen). This turns the second site of the modified Stern-Volmer equation (1) to minor influence, which brings it nearly back to its original form. All other datasheet values were used without variation. Own calibration values obtained at room temperature were used according to section 3. Peaks in Fig. 11 indicate moments of temperature change, the compensation of temperature effect was done by assuming the temperature change as jump.



Fig. 10: SRM in oven with reference temperature measurement (in silicon oil).

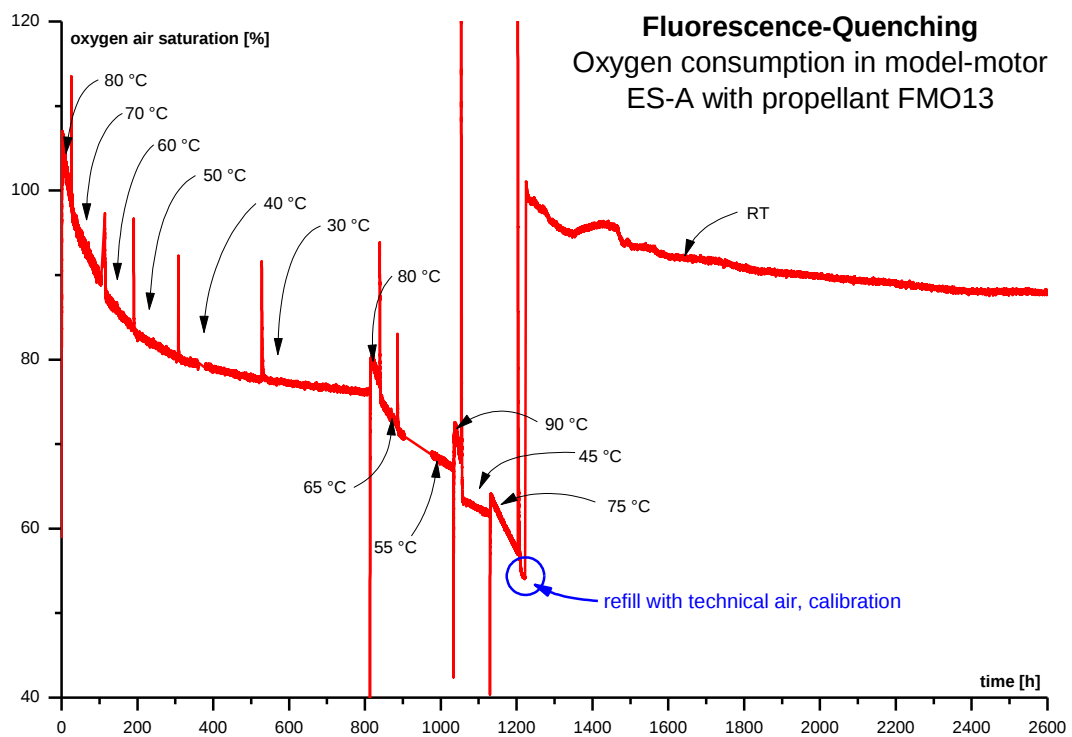


Fig. 11: Temperature compensated oxygen concentration (100 % air saturation equals 20.95 vol-% of oxygen concentration) of SRM "ES-A" filled with FMO13.

The decrease of the oxygen concentration cannot be a cause of improper sealing. Compare to Fig. 11: The experiment started at 80 °C and run downwards in temperature. By this pressure compensation would have happened probably early before the 30 °C step and then, during this 30 °C step the pressure in the system should be lower than ambient. Therefore, the oxygen concentration would either stay constant or increase again due to an influx of ambient air. The opposite is observed; oxygen concentration decrease is still and clearly visible at 30 °C.

For further evaluation, the first section of 80 °C and the 45 °C data were skipped. The 80 °C section is assumed to show some behaviour, which is not in correlation with the second section of 80 °C, with approx. 800 h measurement time. The reason may be that in the early beginning of the high temperature application a bit more exponential then linear concentration course occurs. For the 45 °C data the slope is similar to the slope of 55 °C determined before the 45°C measurement. This is seen erroneous, may be an adjustment error of the oven could be the reason.

The concentration of oxygen from % air saturation to vol-% is done by Eq. (4). With a pressure of 995 mbar at 24 °C (ambient conditions at sealing the SRM) the molar oxygen content can be calculated according to Eq. (5), which is derived from the ideal gas law.

$$[O_{2,Vol\%}] = [O_{2,AirSat}] \cdot \frac{20.95}{100} \quad (4)$$

$$n_{O_2} = \frac{p(T) \cdot [O_{2,Vol\%}] \cdot V}{R \cdot (T - T_0)} \quad (5)$$

$O_{2,Vol\%}$	volume content of molecular oxygen
$O_{2,AirSat}$	saturation ratio of molecular oxygen
n_{O_2}	amount of oxygen molecules
$p(T)$	pressure (temperature dependent)
V	included gas volume (within SRM), see Fig. 3
R	universal gas constant
T	current temperature
T_0	= -273.15 °C

The time course of the molar oxygen content is normalized with its initial value within one temperature section. The decrease in every section is assumed to be linear dependent on time. A linear fit was used to obtain the intersect, and this was used to build the normalized molar concentration ratio.

An important step for further curve fitting was done using Origin v8.5; the dataset seen in Fig. 11 was re-sampled with the function `reduce_ex` (resample factor 5, Y Mean) which generated equidistant x-data and reduced the amount of data by a factor 5. Equidistant data is necessary to avoid over-weighting of sections of otherwise higher sampling rate. After normalizing and shifting of every temperature section to time $t=0$, the final data plot of the oxygen consumption including reaction kinetic can be seen in Fig. 12.

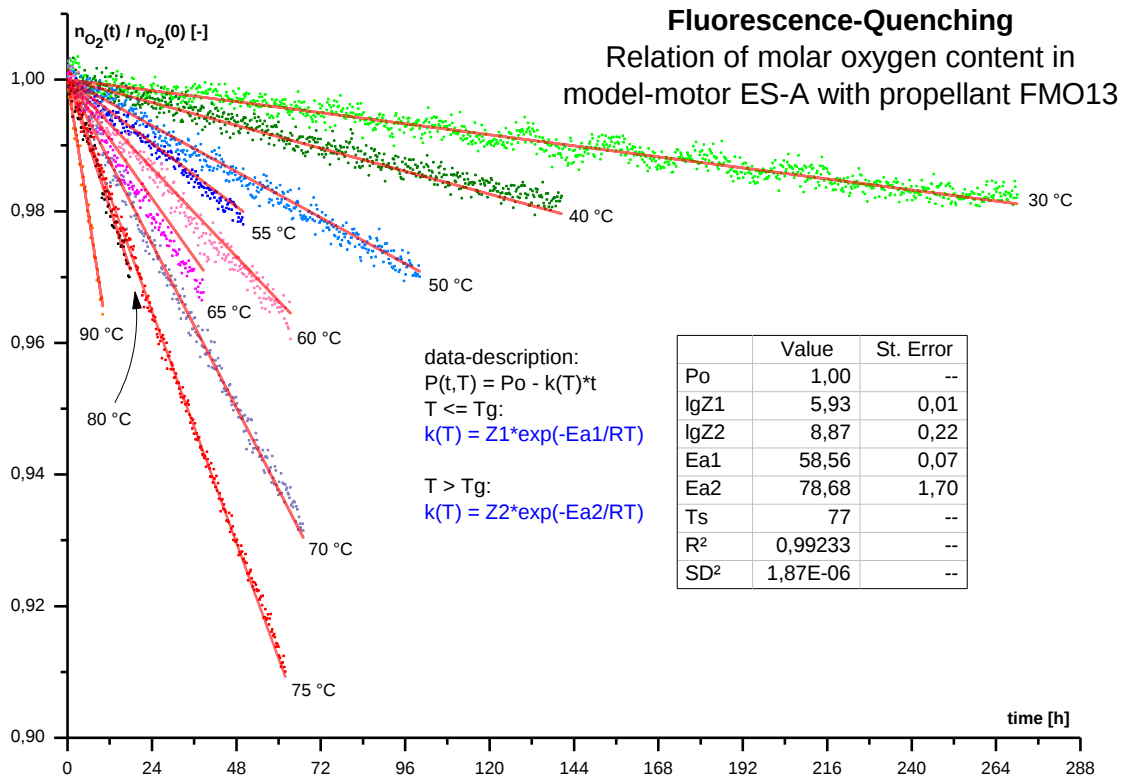


Fig. 12: Decrease of normalized molar oxygen content at 30°C to 90 °C. Description of data with a model of zero-order and using Arrhenius behaviour of the rate constant. A change in activation energy at distinct switching temperature T_s is found. For meaning and choosing of T_s see below.

Generalized van't Hoff and Arrhenius assumptions for temperature dependence of the rate constant and two descriptions of the isothermal data, (1) zero order decrease and (2) first order decrease, were applied to get the reaction rate constants of the oxygen consumption, see Eqs. (6) to (9).

$$P(t,T) = P_o - k_0(T) \cdot t \quad (6)$$

$$P(t,T) = P_o \cdot \exp(k_1(T) \cdot t) \quad (7)$$

$$k_j(T) = Z \cdot \exp\left(\frac{-Ea}{R \cdot T}\right) \quad (8)$$

$$k_j(T) = H \cdot F^{T/\Delta T_F} \quad (9)$$

$P(t,T)$ (general) property (time and temperature-dependent)

P_o property at $t = 0$

$k_i(T)$ reaction rate constant

t time

T Temperature in Kelvin

Ea activation energy

R universal gas constant

Z pre-exponential factor

H van't Hoff pre-factor

F van't Hoff factor

ΔT_F = 10 K

It turned out, that all models describe the consumption with R^2 (coefficient of determination, COD) better than 0.98. It is known that the activation energy for the oxygen reaction in HTPB SRP may increase at above approx. 60 °C. Therefore a fit was applied which optimizes this switching temperature T_s and fit parameters as activation energies and F-factors in the temperature regimes above and below. The following Table 2 and Table 3 gives values for each model and type of temperature parameterization and with and without a T-switching.

Table 2: Kinetic models and temperature parameterisation of the rate constants, assuming a switching temperature T_s . Parameters in each two upper rows refer to temperatures $T < T_s$.

Type of parameterization of rate constant	Model order	T_s [°C]	F [-] lg(H [l/h])	Ea [kJ/mol] lg(Z [l/h])	R^2
Arrhenius	zero	77	-	58.6 ± 0.2	0.9923
				5.93 ± 0.01	
				78.7 ± 1.7 8.87 ± 0.07	
Arrhenius	first	77	-	59.2 ± 0.2	0.9923
				6.04 ± 0.01	
				78.7 ± 1.7 8.89 ± 0.08	
van't Hoff	zero	77	1.93 ± 0.002	-	0.9878
			-12.8 ± 0.01		
			2.1 ± 0.03 -14.1 ± 0.23		
van't Hoff	first	77	1.94 ± 0.002	-	0.9889
			-12.9 ± 0.01		
			2.1 ± 0.03 -14.2 ± 0.03		

Table 3: Kinetic parameters for the two kinetic models applied, without applying a switching temperature T_s .

Type of parameterization of rate constant	Model order	F [-] lg(H [l/h])	Ea [kJ/mol] lg(Z [l/h])	R^2
Arrhenius	zero		58.5 ± 0.08	0.9920
			5.93 ± 0.01	
Arrhenius	first	-	59.1 ± 0.08	0.9923
			6.03 ± 0.01	
van't Hoff	zero	1.92 ± 0.002 -12.74 ± 0.01	-	0.9871
van't Hoff	first	1.94 ± 0.002 -12.82 ± 0.01	-	0.9878

From Fig. 12 a good correlation of the kinetic model can be seen clearly. Merely the experimental data of 60 and 65 °C are described not perfect by a zero-order Arrhenius kind model. But also the other considered models do not improve the description of these data. It is possible, that slight variations of the ageing temperature disturb the description of the experimental data. The measurement of the reference temperature, shown in Fig. 10 was done only for the half of the temperature ranges. A good evidence of temperature effects can

be seen in the 30 °C course in Fig. 12: The sinusoidal shape with a period of approx. 24 h indicates day-night-cycles. Somewhat striking is the fact that without temperature switching the description of the whole data set is as well as with T-switch. One possible explanation is that the lower temperatures comprise more data and determine the parameter fit more than the higher temperatures. The oxygen consumption rate within the motor was determined to 0.023 mmol/d at 60 °C.

4.2 Reference experiment using Raman-spectroscopy

The experimental scatter of the Raman data is much higher than for the fluorescence-quenching data, see Fig. 13. With the objective to obtain reference values for the fluorescence experiment, four temperatures (50, 60, 70 and 80 °C) have been realised. The temperatures were applied in a rising strategy.

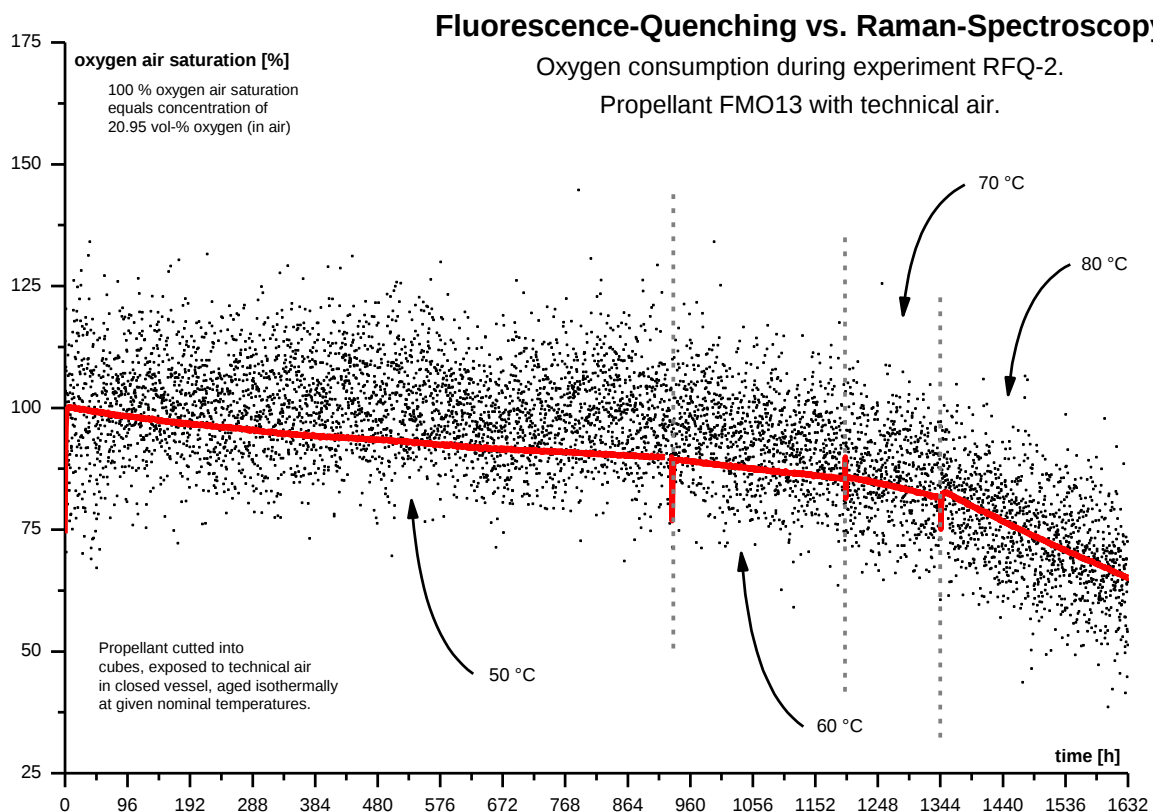


Fig. 13: Result of the experiment named RFQ-2. Plotted as scatter is the Raman result, plotted as (red) line is the fluorescence result (both data raw).

To obtain absolute values for the oxygen concentration the ratio of the peak areas of oxygen and nitrogen was used, assuming a constant concentration of nitrogen during the experiment. This approach made further calibration measurements obsolete. Nevertheless, validation measurements were done using vacuum, pure nitrogen, a mixture of each 50 % oxygen and carbon dioxide and ambient air. See Fig. 14 for a typical spectrum of the atmosphere within the reference cell, filled with technical air and sample material of FMO13.

The experiment was prepared carefully. Sample material of the propellant FMO13 was taken from the core of bulk material, which was closely wrapped with aluminium foil and stored in a glass desiccator, filled in the first time with argon and later on with nitrogen. After cutting the material into cubes of a side length of 4 mm (in the case of experiment RFQ-2), these cubes were exposed to a pure nitrogen atmosphere within a desiccator at elevated temperatures (above 60 °C) to saturate the material with molecular nitrogen by solution. This

optimizes the constancy of the nitrogen level during the experiment later, because otherwise the sample material comes first time in contact with nitrogen during the experiment and nitrogen from the atmosphere is consumed by a migration and solution process. The cubes have been counted during cutting to calculate the sample surface area.

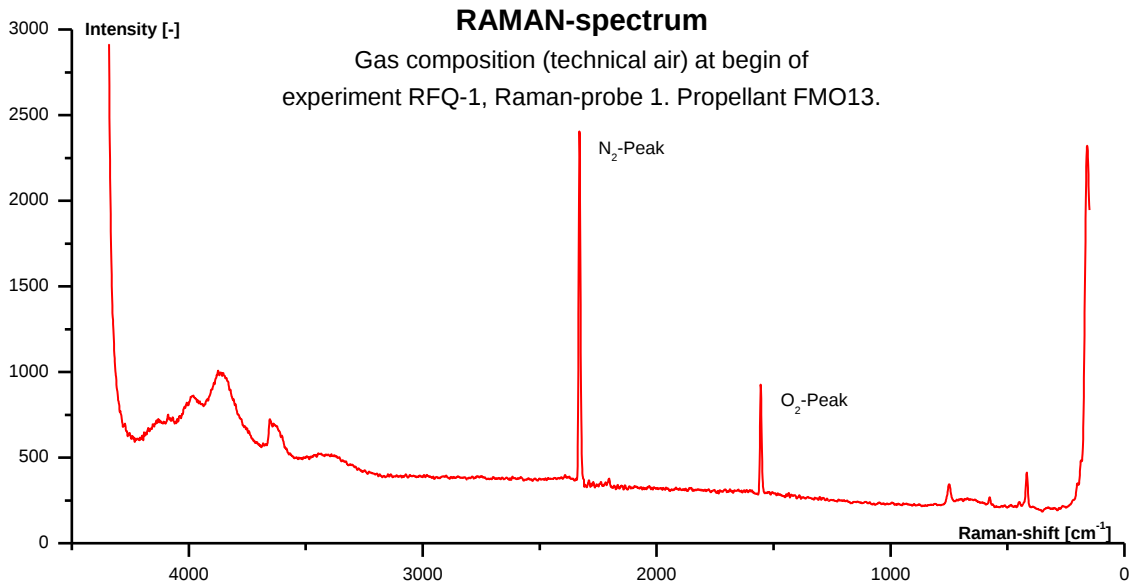


Fig. 14: Raman-spectrum of the atmosphere at the beginning of experiment RFQ-1.

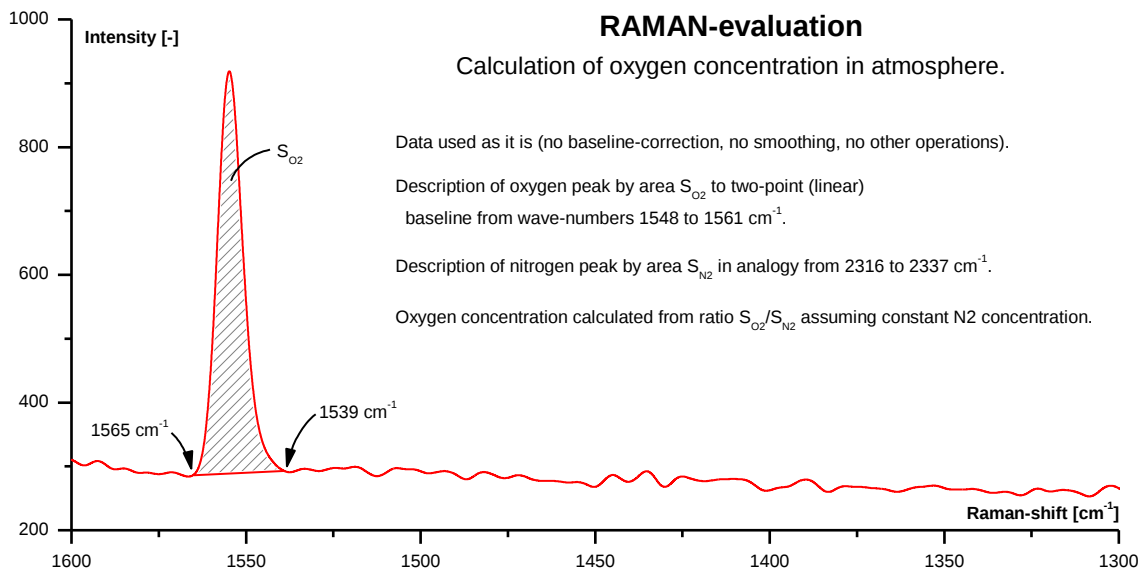


Fig. 15: Calculation of the oxygen concentration from Raman spectra.

After cooling down to room temperature, still protected from oxygen, the sample material was quickly weighted out and brought into the sample container. The sample container was then closed, evacuated and filled with technical air 3 times, to ensure a good knowledge about the gas composition. After this procedure, the valve-system was removed (on slight overpressure) and very quickly replaced by a Swagelok® stopper screw. Due to the overpressure, a negligible gas exchange with ambient air happens. The inner pressure at room temperature is defined by this procedure to be ambient pressure. Then the whole reference cell was placed into a laboratory oven (see again Fig. 8), including the fluorescence-quenching equipment and a temperature sensor. Due to temperature increase the inner pressure rises. Therefore the experiment RFQ-2 runs at small overpressure.

Data evaluation of the Raman measurements was performed applying peak analysis, see Fig. 15. The spectra were used as they are, means no mathematical operations, especially base-line corrections, were done. Smoothing was found not to be effective to reduce the experimental scattering. The peak areas with respect to a 2-point straight baseline were calculated within the limits given in Fig. 15. Those limits were chosen iteratively: When the lowest scatter in the peak surface ratio was obtained, the limits were seen to be best. The ratio of the oxygen peak area to the nitrogen peak area was calculated. From this, the absolute oxygen concentration in vol-% was calculated. With this value the amount of oxygen molecules can be calculated by Eq. (4) and Eq. (5), see more explanations later in this chapter.

$$\frac{2 \cdot M_{u,O_2}}{2 \cdot M_{u,N_2}} \cdot \frac{[O_{2,Vol\%}]}{[N_{2,Vol\%}]} = 0.286 \quad (10)$$

M_{u,O_2} = 15.999 u, atomic mass of oxygen

M_{u,N_2} = 14.007 u, atomic mass of nitrogen

$[O_{2,Vol\%}]$ = 20 %, volume content of molecular oxygen in technical air

$[N_{2,Vol\%}]$ = 80 %, volume content of molecular oxygen in technical air

The Raman intensity is directly proportional to the amount of molecules within the section of measurement, which is the space inside of the Raman probe where the emitter beam runs from the exit of the glass fibre through the gas atmosphere to the mirror (and back). The intensity is in this case nearly independent from pressure or temperature, but dependent from the number of molecules. The expected Raman intensity ratio of O_2/N_2 for the used technical air is in this case given by Eq. (10) to be 0.286. The measured intensity ration with probe one was 0.293 and with probe two 0.255.

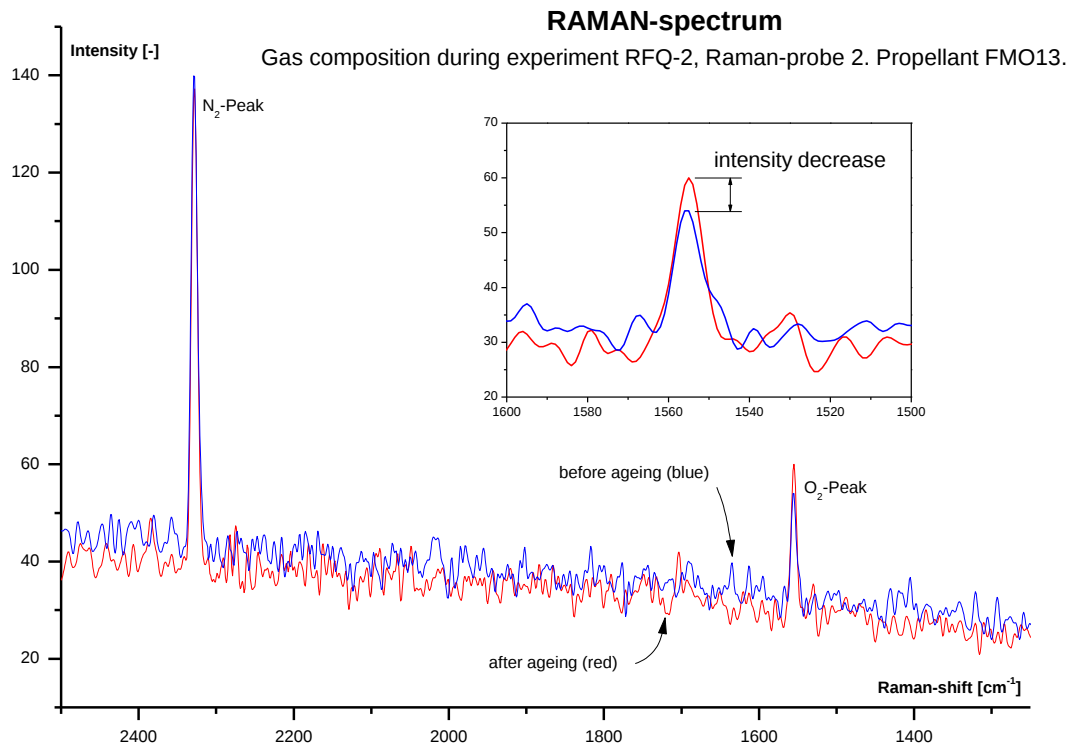


Fig. 16: Decrease of the oxygen peak in experiment RFQ-2 (beginning vs. end).

The decrease of the oxygen content in the atmosphere is shown in the spectra as a decrease of the oxygen peak intensity, see Fig. 16. The nitrogen peak intensity stays constant. The change of the shape of the oxygen peak cannot be explained; maybe it is due to experimental scatter in baseline. The spectra in Fig. 16 were obtained on the early beginning and close to the end of the experiment RFQ-2.

Despite of the low SNR for the oxygen concentration values obtained by Raman-spectroscopy, a fit of the kinetic models makes sense. For that the peak areas of oxygen and nitrogen were normalized to their starting value, in analogy to the method for normalizing the fluorescence-quenching data. See Fig. 17 for the result of the experiment RFQ-2. Clearly visible is the temperature dependence of the oxygen consumption rate. Due to the high scattering a variation of kinetic models is expected to give not more outcome, so just a zero-order Arrhenius-type model was applied.

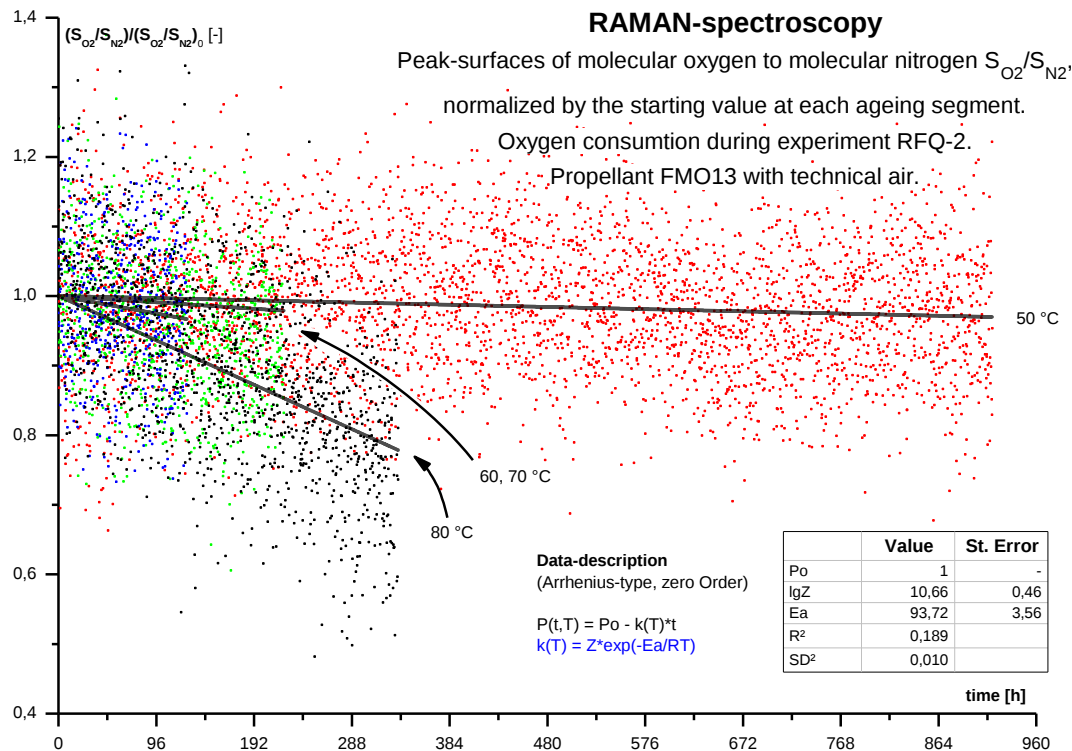


Fig. 17: Modelling of the kinetic of the oxygen decrease during experiment RFQ-2, measured by Raman-spectroscopy.

The reference experiment used Raman-spectroscopy and fluorescence-quenching at the same time in the same chamber. The result of the kinetic modelling of the fluorescence-quenching results is shown in Fig. 18. Note the SNR in direct comparison of Fig. 17 and Fig. 18. Clearly visible in Fig. 18 is a reaction trend of first order, especially in the course of the 80 °C data. The best fit results were obtained when assuming the existence of a switching temperature in the temperature range of 60-70 °C. The fit correlation is event better than for the experiment in the SRM.

From the fluorescence-quenching data within the reference cell an absolute oxygen consumption rate of 0.005 mmol/d was obtained at 60 °C.

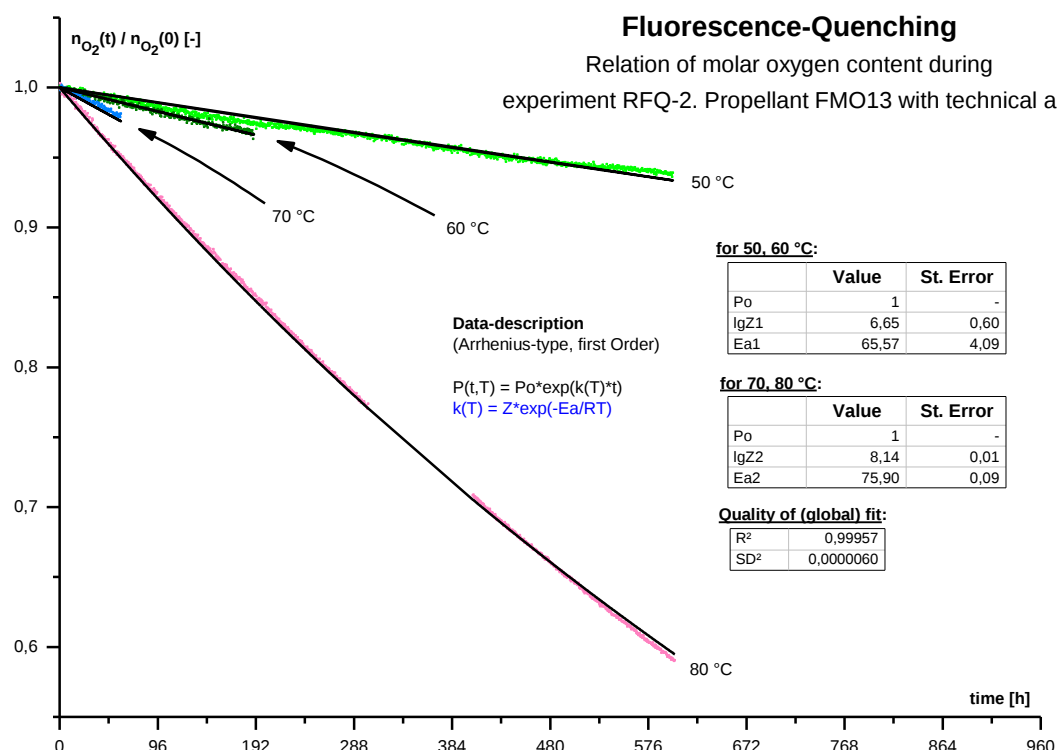


Fig. 18: Modelling of the kinetic of the oxygen decrease during experiment RFQ-2, measured by fluorescence-quenching. Note the application of a switching temperature.

5 Conclusion

The oxygen consumption determined by fluorescence-quenching method within a SRM at elevated temperature levels showed right from the beginning a very good signal-noise-ratio (SNR). By reducing the temperature in steps of 10 K the SNR remained at a level which made a good description of the oxygen consumption possible; even down to near room temperature. Nevertheless, the obtained experimental data in a temperature range from 30 °C to 90 °C can be described very well by kinetic models. Evidence was found that for higher temperatures (above 70-75 °C) the activation energy raises from 59 to 79 kJ/mol for the decrease of molecular oxygen in the atmosphere in the bore of a model SRP. It could be shown that with appropriate preparation and calibration a measurement of the oxygen concentration within a SRM containing HTPB-based SRP delivers a good kinetic model of the oxidative consumption mechanism already after 30 days.

Reference measurements in a specially designed measurement chamber using Raman spectroscopy showed much higher experimental scatter, means lower SNR, which is mainly caused by the low wave-number resolution. The calculation of peak parameters is not very reproducible. Best results were obtained by using the peak area subtracted by a baseline defined directly at the foot point of the peak. With Raman spectroscopy an activation energy of 94 kJ/mol for the consumption of molecular oxygen by SRP was found. Caused by the low SNR, the description of the data by the model was limited. Within the same measurement chamber fluorescence-quenching was applied. Due to higher SNR the kinetic of the consumption could be studied with more confidence. Like in the SRM, evidence was found that for higher temperatures, in this case between 60-70 °C, the activation energy raises from 66 to 76 kJ/mol, which is in good accordance with the values obtained from the measurements directly in the SRM.

From the observation, that for cut sample material in the reference experiment and for smooth-surface material inside of the SRM the kinetic of the oxygen consumption by the SRP follows the same model one can conclude that the surface structure has not much influence on the main mechanism, which consumes the oxygen. When comparing absolute values of the consumption rate one must take into account, that the air-volume to sample-surface area ratio in the reference experiment is smaller by factor 6 compared to the situation in the SRM. From these numbers a higher consumption rate in the reference experiment could be expected, but is not detectable. The observation is the opposite: the absolute consumption rate in the reference experiment is smaller by factor 4.6 - like the air volume to sample-mass ratio would suggest; this ratio is factor 3 higher for the reference experiment than for the SRM. This consideration leads to the conclusion, that the oxygen consumption is more dependent from the volume (or mass) of the sample material, than from the surface area. This means, that in case of the experimental geometries the depth of oxygen diffusion is less limited.

It was found, that the fan, implemented into the reference cell, did not affect the measurements. The molecular movements within the atmosphere around the sample material seem to mix the gas efficiently enough.

Three of four measurements with the reference cell show evidence of leakage. The sealing of the Raman-probe itself should be checked.

For both methods, the Raman-spectroscopy and fluorescence-quenching, an important error source may be the effect of the plasticizer DOA. It is degassing in small amounts from the propellant and deposit on surfaces, like the oxygen sensor spot, where it could migrate into the matrix or deposit on the mirror in the Raman probe. Both effects are unavoidable.

For future activities it is planned to establish a method for measuring diffusion coefficients for oxygen into SRP. Another activity to complete is the comparison to chemiluminescence measurements, which are already made.

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Abbreviations

Al	aluminium
AP	ammonium perchlorate
BET	Brunauer–Emmett–Teller (theory to explain physical adsorption)
CRP	composite rocket propellant
DMA	dynamic-mechanical analysis
DOA	dioctyladipate, plasticizer
EPDM	
FMO	name of a CRP-series
GC	gas-chromatography
HFC	heat-flow microcalorimetry
HTPB	hydroxyl-terminated polybutadiene
HX 878	Tepanol, bonding agent
IPDI	isophorone diisocyanate, curing agent
Irganox 565	antioxidant
IST	in-service-time
NATO	North Atlantic Treaty Organization
NC	nitrocellulose
NPT	national pipe thread
PID	proportional-integral-derivative
PTFE	Polytetrafluoroethylene (teflon)
PU	polyurethane
R45M, R45HT	quality index of HTPB types
RFQ	own abbr. for Raman-Fluorescence-Quenching-measurement
SEM	scanning electron microscopy
SRM	solid rocket motor
SNR	signal to noise ratio
STANAG	(NATO) standardization agreement
TPB	triphenyl bismuth, curing catalyst

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