



Analysis of passive calorimetric probe measurements at high energy influxes

Thorben Kewitz^{1*} , Maik Fröhlich² and Holger Kersten¹

* Correspondence:

kewitz@physik.uni-kiel.de

¹Institute of Experimental and Applied Physics, Kiel University, Kiel 24098, Germany

Full list of author information is available at the end of the article

Abstract

High energy influxes increase the complexity of passive calorimetric probe measurements because of an increasing temperature of the surrounding materials like the probe holder. This leads to a distinctively different evolution of the probe temperature compared to low energy influxes. Different established methods for the analysis of passive calorimetric probe data are presented and it is shown that they are not applicable for high energy influx measurements resulting in the requirement of a novel analysis approach. Such an approach is given in this paper by the combination of the exponential and the linear method. The high energy influx measurements are studied for a commercial atmospheric pressure plasma jet, in order to illustrate our suggested modified approach.

Keywords: Calorimetric probe, High energy influx, Atmospheric pressure plasma jet, Plasma diagnostics

Introduction

Atmospheric pressure plasma jets are used for cleaning, activation and thin film coating of metal, plastics and other materials [1, 2]. But often they have a large energy flux onto surfaces because of input powers in the kW range. As the thermal stress of a substrate is a key parameter in many different plasma applications, in particular, for temperature-sensitive materials, detailed knowledge is needed for the optimization of processes involving these sources. The thermal conditions not only define process limitations, but also influence the quality of coatings [3]. Yet, atmospheric plasma sources with a high energy influx in the order of 100 W/cm^2 towards substrate surfaces offer some advantages compared to low power sources ($<1 \text{ W/cm}^2$), e.g., faster treatments of substrates and effective use of precursors.

Calorimetric probes are a well-known and widespread diagnostic tool for the determination of the energy influx [4, 5]. They can be divided into active and passive calorimetric probes. The active probes are heated to a constant temperature and the heating power is recorded. Any additional energy influx from a plasma source results directly in a reduced heating power. However, only energy influxes smaller than the heating power can be measured, which puts a limit to this diagnostic. The limit of the probe used so far are a few watts per square centimeter and can, therefore, not be used for high energy influxes [6]. The passive probes can be distinguished for different principles, again. For example, the probes are exposed to the energy source on the one side

of the probe and cooled on the other side until a stationary temperature distribution is reached [7]. This leads to a spatial temperature gradient along the probe from which the energy influx can be derived. The other principle uses smaller probes, which are considered to have a negligible temperature gradient in the heated part of the probe during the plasma interaction. These probes based on temporal changes of the temperature have been used in many different designs for versatile processes, mostly at low pressure and small energy flux applications. A suitable review can be found in [5].

It was already shown that for the investigation of atmospheric pressure plasma jets with a large power consumption changes in the design of the probe are necessary [8]. These adaptations allow to handle the high mechanical and thermal stress of the probe induced by the investigated high power atmospheric pressure plasma jet from the company Plasmacreat.

In this present study we will focus on the analysis of the results obtained with modified passive probes. First, we explain the well-known linear and exponential methods [4, 9–11] and the underlying assumptions in detail, before we show for a typical measurement why these methods are not suitable for energy influxes in the order of 100 W/cm². Finally, we introduce a novel method by combining the linear and the exponential methods and show that this approach is suitable for the analysis of high energy influxes by a passive calorimetric probe.

Basics of the analytical method at low energy fluxes

The basis for all the common methods for the analysis of passive calorimetric probe measurements is the consideration of temporal temperature changes during the heating and the cooling phase of the calorimetric probe [9]:

$$C_p \frac{dT_p}{dt} = P_{in} - P_{out} \quad (1)$$

with the heat capacity of the probe C_p , the time derivative of the probe temperature T_p . P_{in} is the net incoming power containing the heating processes as well as losses due to plasma-wall-interactions. A list of the various contributions to the thermal energy balance at the substrate (probe) can be found in [12, 13]. P_{out} , on the other hand, includes all loss processes dependent on the rising temperature of the probe. The processes are heat radiation (Stefan-Boltzmann law)

$$P_{rad} = \varepsilon \sigma A_p (T_p^4 - T_{eq}^4), \quad (2)$$

with the emissivity ε , the Stefan-Boltzmann constant σ , the area of the probe A_p and the equilibrium temperature T_{eq} and thermal conduction

$$P_{cond} = c(T_p - T_{eq}), \quad (3)$$

with a constant c depending on the material and geometry of the probe.

It includes, furthermore, the virtual reduction of the incoming power due to higher substrate temperatures. This reduction is often considered to be a loss in order to distinguish this effect from any other changes of the energy influx [4, 10]. As soon as the substrate temperature rises, the contributions of the total energy flux to the substrate which are dependent on the substrate temperature decline, generally. For example, under atmospheric pressure one of these contributions is that of the heated neutral gas.

The energy transferred from the gas to the substrate will diminish with a rising substrate temperature.

At low pressure free convection can be neglected. When using atmospheric pressure plasma jets, forced convection, which can be treated linearly analog to thermal conduction, may become dominant during the plasma treatment.

The three loss processes, radiation, conduction, and convection, are also those which are present in the cooling phase after plasma treatment. Here, the convection losses are dependent on the experimental conditions. If the gas flow is switched off together with the plasma or if the plasma jet is moved away from the probe, free convection is present. If the gas flow is still on, the losses caused by forced convection depend on the temperature of the gas.

The incoming power can be determined by a comparison of the change of temperature during the heating ($P_{in} - P_{out}$, plasma/energy influx on, eq. 4.1) and the cooling phase (P'_{out} , plasma/energy influx off, eq. 4.2) leading to eq. 4.3:

$$C_p \left(\frac{dT_p}{dt} \right)_{heat} = P_{in} - P_{out} \quad (4.1)$$

$$C_p \left(\frac{dT_p}{dt} \right)_{cool} = -P'_{out} \quad (4.2)$$

$$P_{in} = C_p \left(\left(\frac{dT_p}{dt} \right)_{heat} - \left(\frac{dT_p}{dt} \right)_{cool} \right) + (P_{out} - P'_{out}) \quad (4.3)$$

It is important to point out that the power loss functions during the two phases $P_{out}(T_p)$ and $P'_{out}(T_p)$ are not necessarily the same. A crucial point for the losses to remain the same is the reduction of the incoming power due to higher substrate temperatures. In the case of a plasma jet this loss is mainly caused by the temperature difference between the probe and the neutral gas. As soon as the probe temperature rises, the difference becomes smaller and the incoming power is reduced. To mirror this effect during the cooling phase, a gas flow equally large to that one during the heating phase and at equilibrium temperature has to be applied. However, this is often not achievable due to residual heat in the jet or other effects on the gas temperature. Turning the gas flow off leads to free convection and, thereby, again to different power loss contributions.

Another issue is the temperature of the surrounding, i.e., the probe holder. The power losses in eqs. 2 and 3 are dependent on this temperature, which is the equilibrium temperature T_{eq} at the beginning of the treatment. If the probe holder heats up during the measurement these losses are no longer solely dependent on the probe temperature T_p . Hence, a time dependent component is introduced and, therefore, the power loss functions $P_{out}(T_p)$ and $P'_{out}(T_p)$ differ from each another.

To illustrate these relations and the consequences for the measurement of high energy influxes, we start with the methods used for the analysis of small energy influxes and discuss their applicability to high energy influxes.

The simplest approach to apply the relation given in eq. 4.3 is the linear method. At the beginning of the heating curve at the equilibrium temperature T_{eq} the losses are negligible and the energy influx is proportional to the slope of the temperature curve leading to [9]:

$$P_{in} = C_p \left(\frac{dT_p}{dt} \right)_{heat} \Big|_{T=T_{eq}} \quad (5)$$

Since this method is applied at the beginning of the heating curve, the incoming power should be fully applied in a short time and the recording frequency of the probe temperature should be sufficiently high to minimize uncertainties for the determination of the slope $\left(\frac{dT_p}{dt} \right)_{heat}$. For higher energy influxes the time, where the probe temperature is close to the equilibrium temperature, becomes very short and it is not always possible to apply the full power to the probe in the time available. This may be attributed to a starting phase of the source plasma or moving it over the probe if it was started elsewhere to account for the starting phase. There will always be a short time where the probe is exposed only to a fraction of the total energy flux of the source and where it is already heated up.

Another method is the exponential analysis. With the assumptions of a constant incoming power, linear loss terms, and a constant temperature for the surrounding of the probe the shape of the signal for heating and cooling phases will be exponential [9, 10]:

$$T_{p,heat}(t) = \left(T_{eq} + \frac{P_{in}}{a} \right) - \left(\frac{P_{in}}{a} \right) \exp\left(-\frac{a}{C_p} t \right) \quad (6.1)$$

$$T_{p,cool}(t) = T_{eq} + (T_{p,st} - T_{eq}) \exp\left(-\frac{a}{C_p} t \right) \quad (6.2)$$

Here a is the constant for the linear cooling processes and $T_{p,st}$ the temperature of the probe at the beginning of the cooling phase.

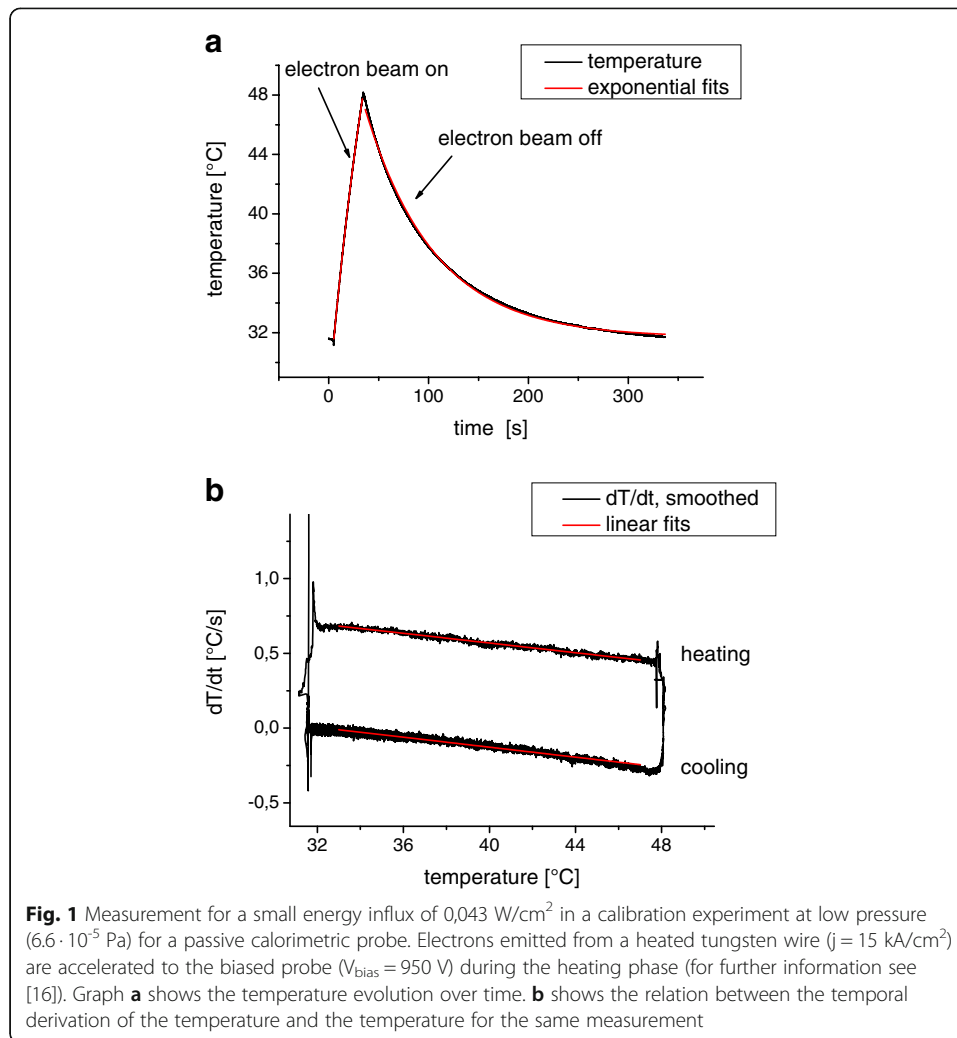
Because of the constant temperature of the surroundings, i.e., T_{eq} , the power loss functions $P_{out}(T_p)$ and $P'_{out}(T_p)$ are equal and cancel each other out (eq. 4.3) leading to [4]:

$$P_{in} = C_p \left(\left(\frac{dT_p}{dt} \right)_{heat} - \left(\frac{dT_p}{dt} \right)_{cool} \right) \quad (7)$$

In this case, the incoming power can be simply calculated with the difference of the time derivatives of the temperature $\dot{T}_p = \frac{dT_p}{dt}$ during the heating and the cooling phase (Fig. 1a). Fig. 1b shows this relation for an exemplary measurement in a low pressure calibration experiment with an electron beam. It can be seen, that the curves of \dot{T}_p for the heating and cooling phase are linear and parallel, so that their difference is roughly constant.

The assumptions made in this case are valid for short measurements with small energy influxes where the temperature of the surrounding materials, i.e., the probe holder, does not change significantly and for probe temperatures where heat loss by radiation is negligible.

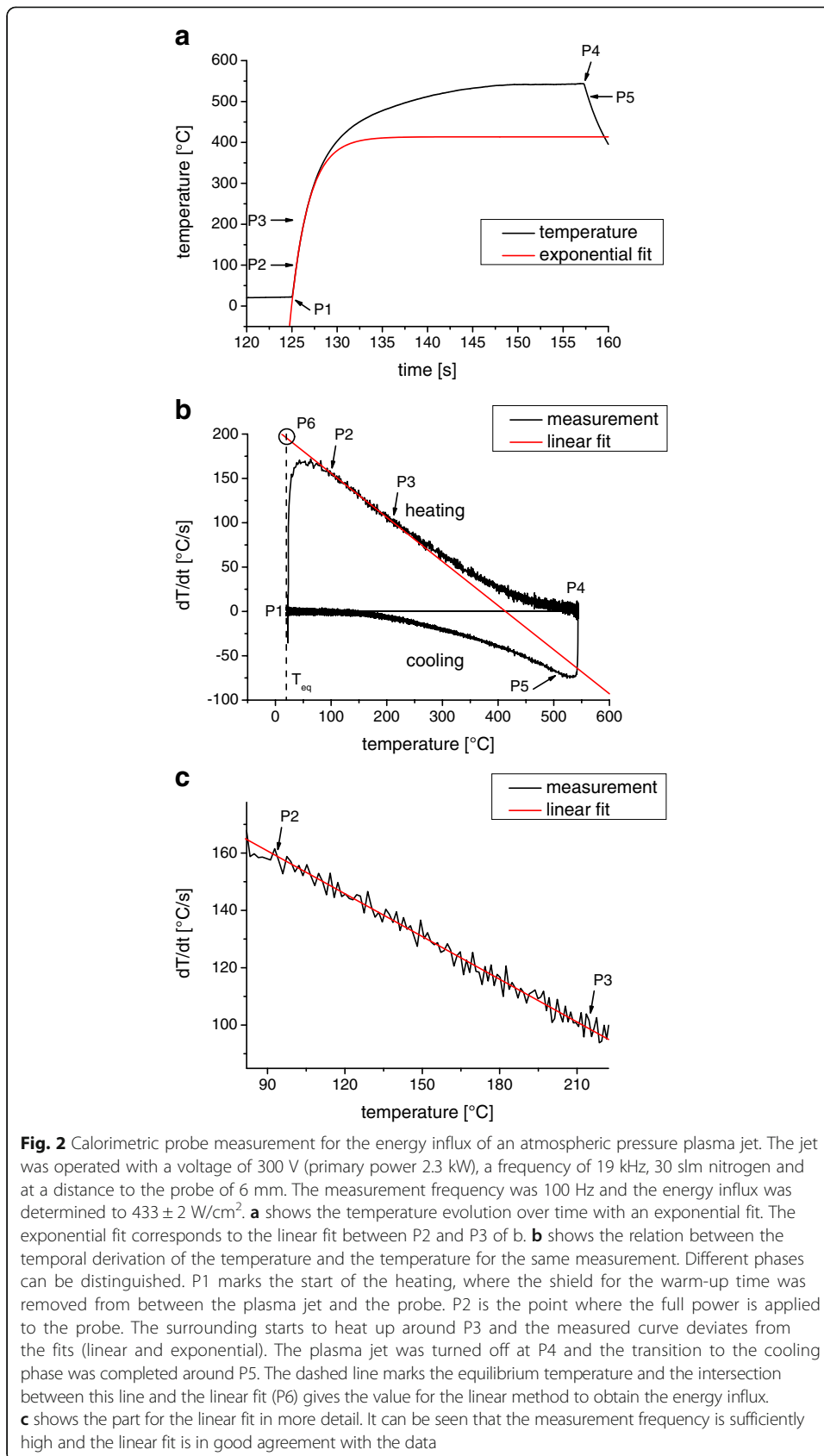
If the probe is used for measurements at higher temperatures, i. e. heated up by sources with high energy influx, thermal radiation becomes relevant and the energy losses can no longer be assumed to be linear (see eq. 2). But, if the energy losses are solely dependent on the probe temperature (constant T_{eq}), the function of the power losses P_{out} represented by the cooling curve \dot{T}_p is still the same for each energy influx measurement. Therefore, eq. 7 can be applied [12].



However, if plasma sources with a high energy influx onto substrates are used, the boundary conditions change. The assumption inherent to the cases above that the power losses are only dependent on the probe temperature can only be made if the surroundings of the probe, i.e., the probe holder, are at equilibrium temperature T_{eq} . But due to the high energies the temperature of the holder may increase remarkably during the treatment. Hence, the temperature T_{eq} in eqs. 2 and 3 is time dependent and, thereby, the power loss function P_{out} . This means that the power loss functions $P_{out}(T_p)$ and $P'_{out}(T_p)$ in eqs. 4.1 and 4.2 are not the same. As a consequence, eq. 7 can no longer be used for the whole measurement and the method has to be modified.

Modified analytical method at high energy fluxes and experimental verification for plasma jet operation

The concerns raised in the discussion of the linear and exponential methods concerning high energy influx measurements are illustrated by a typical measurement for high energy influx in Fig. 2. This measurement was performed at the atmospheric pressure plasma jet system from the company Plasmamatreat [14] consisting of a FG5001 generator, a HTR12 transformer and a RD1004 nozzle (similar to [15]). A metal sheet



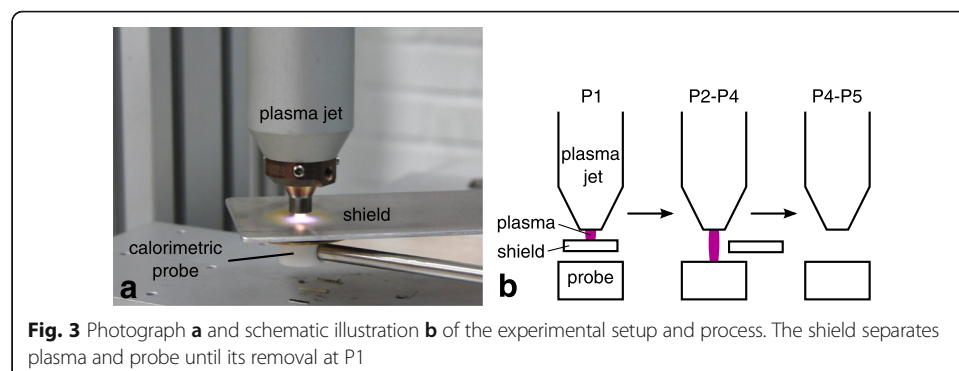
positioned in between the plasma jet and the probe is used to shield the probe during the warm-up time of the jet (see Fig. 3). Once stable conditions are reached the metal sheet is removed and the plasma jet interacts with the probe (P1). As the gas flow does not adjust immediately to the new geometry, the incoming power rises between P1 and P2 until, again, stable conditions are reached and the incoming power is fully applied at P2. From this point on until the point marked with P3 the loss terms are linear, resulting in a linear decrease of \dot{T}_p over T_p , indicating that the surrounding is still at T_{eq} and thermal radiation can be neglected (P2 and P3 are chosen as the limits of this linear decrease). At P3 the temperature of the surrounding starts to increase significantly and the curve deviates from the linear fit (red line) to higher values. This process surpasses also the increasing thermal radiation which should let the measured curve deviate to smaller values compared to the linear fit. P4 marks the time where the plasma jet is switched off and the beginning of the transition phase to the cooling curve which starts at P5.

The two methods described so far depend on a constant temperature T_{eq} of the surrounding. This temperature can be considered as constant between P1 and approximately P3 and also between P4 and P5, because of the short time between these two points.

Due to the changing temperature of the surrounding after P3 the curves do not have an exponential shape and the exponential method cannot be applied. The same applies to the curve before P3, because there is no corresponding part in the cooling curve with the same temperature of the surrounding.

The beginning of the heating phase was already considered for the linear method. The consequences of the concerns mentioned for the use of this method for high energy influxes can be seen clearly in Fig. 2b. The probe temperature is already around 100 °C when the full power is applied to the probe (P2) and the losses cannot be neglected.

The second area, where the temperature of the surrounding can be assumed as constant, the transition between the heating and the cooling phase (P4-P5) is also complex if plasma jets are used. The difficulties to get the same power losses were discussed above. The consequences can again be recognized in Fig. 2b. The decrease after P4 is much smaller than the increase after P1 due to residual heat in the gas flow and can, thus, not be used for the measurement of the energy influx. In conclusion, both, the



linear and the exponential method cannot be used for the analysis of the energy influx in this case.

So, we have shown that the established methods lead to remarkable errors in the determination of the energy influx in this case. Therefore, a modified method is presented in the following.

To overcome the difficulties mentioned, we decided to take the part of the heating curve where $P_{out}(T_p)$ is linear (see Fig. 2b and c between P2 and P3 and compare to the exponential method) and extrapolate the linear fit to the equilibrium temperature (see Fig. 2b at P6). This procedure results in the slope of the temperature curve which we would get at equilibrium temperature if the full power would be applied to the probe immediately and this value is exactly what is used for the linear method. Therefore, we apply the linear method (eq. 5) to obtain the energy influx of $433 \pm 2 \text{ W/cm}^2$ in the given experiment. An additional uncertainty of about 10% is induced by the calibration of the probe. Using the Gaussian profile of the jet obtained at the same parameters with air (standard deviations of $3.35 \pm 0.06 \text{ mm}$ and $3.47 \pm 0.06 \text{ mm}$ in x - and y -directions [8]) and regarding the probe diameter of 5 mm, this results in a total energy flux from the jet of $1.61 \pm 0.16 \text{ kW}$. This value is comprehensible considering the primary power of 2.3 kW used for this experiment, since a lower value was expected due to different losses in the plasma jet system and only a fraction of the total energy is transferred to the surface. A closer look at the part for the linear fit is presented in Fig. 2c. It illustrates in more detail that the linear fit is in good agreement with the data and that the amount of measured points is sufficient for this method.

Conclusion

The passive calorimetric probe measurements at high energy influxes show distinctively different temperature evolutions compared to measurements at low energy influxes. The slopes of the heating and cooling curves differ substantially from each other due to the changing temperature of the surrounding material. The analysis methods used so far in the literature are based either on a constant temperature T_{eq} of this surrounding or, with the linear method, a fast application of the full power to the measuring probe. Since neither of these conditions is fulfilled by the investigated atmospheric pressure plasma jet a combination of the exponential and the linear method was used. This combination omits the necessity of a fast application of the full power by using the exponential part of the heating curve and in the same time does not require the surrounding to be close to the equilibrium temperature for a long time. The successful application for the investigation of energy fluxes in the order of 100 W/cm^2 was presented.

Acknowledgements

The authors would like to thank the company Plasmatreteat for supplying the plasma jet system. The authors would also like to thank V. Rohwer, M. Poser, and T. Riedel for the technical assistance and F. Haase for the calibration measurement (Fig. 1a and b). This work was supported by the German Federal Ministry of Education and Research (BMBF) under Project FKZ: 13 N12220.

Authors' contributions

All authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

Author details

¹Institute of Experimental and Applied Physics, Kiel University, Kiel 24098, Germany. ²Leibniz Institute for Plasma Science and Technology, Greifswald 17489, Germany.

Received: 11 July 2016 Accepted: 19 December 2016

Published online: 19 January 2017

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