AN ATTEMPT TO ESTIMATE THE UNCERTAINTY OF MEASUREMENTS OF PARAMETERS OF PARTICULATE MATTER OXIDATION KINETICS

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Summary

In this paper, an attempt has been made to estimate the uncertainty of measurements of the parameters that describe the kinetics of oxidation of the particulate matter (PM) produced during fuel combustion in compression ignition (CI) engines. The kinetics of the process is characterized by two basic parameters: activation energy E_a and PM oxidation rate constant k_0. One of the methods to determine the values of these quantities is based on gravimetric measurements of the decrement of mass of the particulate matter when being burnt. The course of the PM oxidation process depends with considerable significance on the repeatability of process conditions, which affects the values of the kinetics parameters being determined. The parameters Ea and k_0 are of fundamental importance at simulation tests and at analysing the PM oxidation (combustion) process; they are also vital to developing the methods of reconditioning automotive exhaust gas filters. It is essential that for the above needs, the parameters E_a and k_0 should be determined with a definite level of reliability; this means that the measurement results must be subjected to a statistical analysis. A procedure of statistical analysis of measurement results and the estimated values of the above parameters, obtained from experimental investigations of the kinetics of the PM oxidation process, have been presented below.

About 1 000 realizations were recorded in various process conditions on a test stand for gravimetric investigations of the PM oxidation process. For the needs of this paper, a series of measurement results was selected from that, based on predefined criteria. The selected results were subjected to a Dixon's Q test, which is to eliminate outliers from the data set. For the normal probability distribution of data and a specific confidence level having been assumed, the uncertainty level was calculated and the measurement result was specified as an arithmetic mean of the series of individual results with the corresponding uncertainty interval. In result of the statistical analysis, reliable values of the parameters E_a and k_0 and of their uncertainty were determined with the assumed confidence level.

For the calculated E_a and k_0 parameter values to be additionally verified, they were subjected to a statistical test in order to eliminate those being outside of the range determined for the assumed confidence level and for the standard deviation of the series of measurements. The test confirmed

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the uncertainty to have been estimated correctly; moreover, conclusions from this work could be formulated based on this test.

Keywords: particulate matter, oxidation, kinetics, measurement uncertainty

1. Introduction

There are many methods at present that make it possible to assess the substantive correctness of the measurements carried out within the research and development works being done. In market applications, such methods must often be employed to show without any bias that the tests carried out by a laboratory are trustworthy and reliable. The methods that guarantee high quality of the tests include e.g. the ensuring of coherence of measurements, validation of the test method used, and estimation of uncertainty of the measurements made. Each of these methods describes a separate feature of the measurement.

The assessment of coherence of the measurements made and the validation of the test method used make it possible to answer a question whether the measurements were carried out in a way ensuring the traceability of the quantities measured to the international system of measurement standards and whether the test method used gives results comparable with results obtainable from other methods (e.g. the standard methods). On the other hand, the analysis of uncertainty of measurements makes it possible to determine (often in probabilistic terms) the statistical reliability of the measurements.

Due to a specific nature of the measurements and usually a limited time and scope of the tests, the estimation of uncertainty of measurements is often replaced with a simplified calculus of errors. At the experiments carried out for research or innovation purposes, the attention is in most cases focused on the experiment results obtained, on the interpretation of such results, and on the conclusions drawn from the result analysis; the analysis of the reliability of the results obtained usually is not considered among the issues of top priority.

In respect of the estimation of uncertainty of measurement results, the greatest difficulties are encountered at the multi-parameter cross-sectional research works where results depend on numerous factors and the research method adopted. The research works of this kind include experimental gravimetric investigations of the kinetics of particulate matter oxidation. In the relevant literature available [e.g. 2, 3, 4], simulation tests based on the assumed values of parameters of the oxidation kinetics have been described. The values adopted for the simulation models of reconditioning of exhaust gas filters required experimental verification. Investigations of parameters of the PM oxidation kinetics were carried out in Poland within research project No. 4 T12D 026 29 sponsored by the State Committee for Scientific Research. In the work reports published to date, partial results have been given in publications [6–17] and the overall results have been presented in publication [1], the latter including correlations between the process conditions (simulating the real conditions prevailing during the reconditioning of a PM filter) and the parameters of the PM oxidation kinetics. The large number of measurements made and the numerous values of oxidation kinetics parameters determined from the measurements enable the data obtained to be subjected to a statistical analysis and the uncertainty of the values of parameters E_a and k_0 to be estimated.

2. Gravimetric investigations of parameters of the particulate matter oxidation kinetics

The procedure of investigation of the PM oxidation kinetics with the use of the gravimetric method and a test stand suitable for applying such a method has been described in details in publication [1]. A brief description of this method and of the construction and functioning of the unique test stand used for this purpose has been provided below.

2.1. Method of gravimetric investigations of the PM oxidation kinetics

In most cases, the kinetics of the process of PM oxidation in automotive exhaust gas filters is described by one of the forms of the empirical Arrhenius equation

$$k = k_0 \cdot r_{O_2} \cdot \exp\left(-\frac{E_a}{\overline{R} \cdot T}\right) \tag{2.1}$$

where:

k	– PM oxidation rate;
k_0 [s^{-1}]	– PM oxidation rate constant;
r_{O2} [kmol O_2/kmol of oxidizer]	– molar (volumetric) fraction of oxygen in the oxidizer;
E_a [MJ/kmol]	– PM oxidation activation energy;
$\overline{R}$ [MJ/(kmol×K)]	– universal gas constant;
T [K]	– temperature of isothermal oxidation.

Individual quantities represented in the Arrhenius equation (2.1) characterize the process conditions in which the PM oxidation takes place.

An important assumption is the defining of the temperature that is taken into account in the exponent (formula 2.1). In report [1] and in subsequent publications, an assumption has been made that the temperature T present in equation (2.1) should mean the oxidizer temperature T_u. Such an assumption stems from the observation of process temperatures: the process is started and initially runs isothermally at the temperature T_u, while this is the process stage that is used in the procedure of determining the values of E_a and k_0. Therefore, when substituting T_u for T in formula (2.1) and taking a logarithm from the equation, we obtain the following:

$$\ln k = \ln\left(k_0 \cdot r_{O_2}\right) - \frac{E_a}{\overline{R}} \cdot \frac{1}{T_u} \tag{2.2}$$

If the following substitutions are applied:

$$y = \ln k \tag{2.3a}$$

$$x = \frac{1}{T_u} \tag{2.3b}$$

$$a = \left(-\frac{E_a}{R}\right) \tag{2.3c}$$

$$b = \ln\left(k_0 \cdot r_{O_2}\right) \tag{2.3d}$$

then equation (2.2) may be transformed into a linear form

$$y = a \cdot x + b \tag{2.4}$$

The above procedure was described in e.g. [5] and it was the main factor that gave grounds for adopting the gravimetric approach to the investigations of the kinetics of the PM oxidation. When analysing substitutions (2.3), we may notice that the quantities to be found in formula (2.4) are the slope a of the straight line and the free term (intercept) b, while values x and y are directly measured during the experiment.

The rate of PM oxidation in given process conditions can be calculated from the following:

$$k = \frac{\dfrac{m_{PMk} - m_{PMp}}{m_{PMj}}}{\Delta t} \tag{2.5}$$

where:
m_{PMp} [g] – initial particulate matter mass;
m_{PMk} [g] – final particulate matter mass;
m_{PMj} = 1 g – reference particulate matter mass;
Δt [s] – time needed for the oxidation of the PM mass $\Delta_{mPM} = m_{PMk} - m_{PMp}$.

In formula (2.5), there is a term m_{PMj} = 1 g, which makes it possible for the PM oxidation rate k and the PM oxidation rate constant k_0 to be treated as independent of the initial PM mass. Thanks to adopting m_{PMj} = 1 g, the results obtained may be considered in relation to any mass of the particulate matter undergoing the oxidation process.

For the E_a and k_0 parameter values to be determined on the grounds of equation (2.4), at least two experiments with PM oxidation must be carried out at two different temperatures, with the other process conditions being kept unchanged. In result of the two experiments, the x and y values in equation (2.4) are obtained. A pair of the E_a and k_0 values is obtained by solving a system of two equations with two variables. In general, n experiments carried out at n different temperatures with all the other process conditions kept unchanged may produce n – 1 pairs of the E_a and k_0 parameter values.

2.2. Test stand for gravimetric investigations of the PM oxidation kinetics

For the needs of carrying out the procedure described above, a test stand for gravimetric investigations of the PM oxidation kinetics was built within research project No. 4 T12D 026 29 sponsored by the State Committee for Scientific Research (Fig. 2.1). About 1 000 experiments were carried out on this stand in various process conditions, which were arbitrarily defined by the user.

A schematic diagram of the measuring probe has been presented in Fig. 2.2, which shows a test specimen placed on the probe and thermocouples (marked in the diagram) used for measuring the oxidizer temperature, situated immediately upstream of the specimen (Tu) and over the specimen (T2–T5). The test specimen was prepared by applying a PM layer onto the surface of a specimen base (filtering material taken from an original filter).

The test stand shown in Fig. 2.1 made it possible to carry out measurements on specimens cut out from filtering monoliths, which were made from cordierite ceramics (designated by

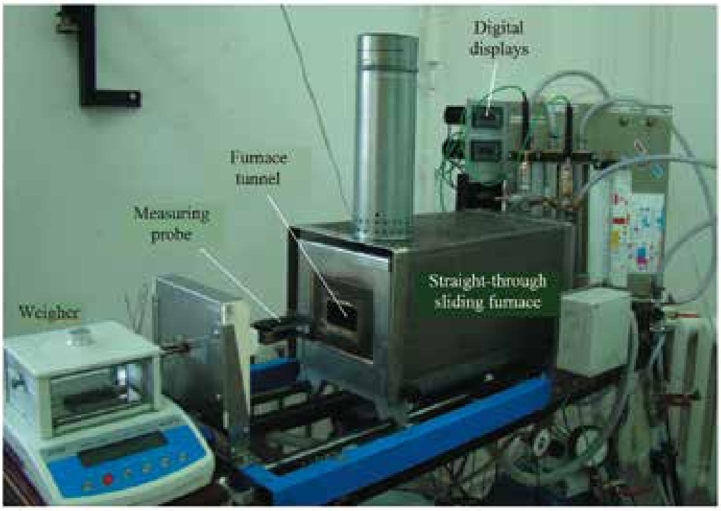

Fig. 2.1. General view of the test stand for gravimetric investigations of the PM oxidation kinetics [16]

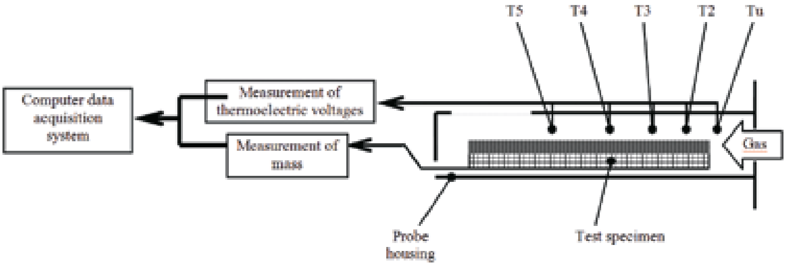

Fig. 2.2. Schematic diagram of the measuring probe with a test specimen [16]

CKF) or from silicon carbide (SiC). A view of the specimens made from cordierite ceramics and silicon carbide has been presented in Figs. 2.3a and 2.3b, respectively.

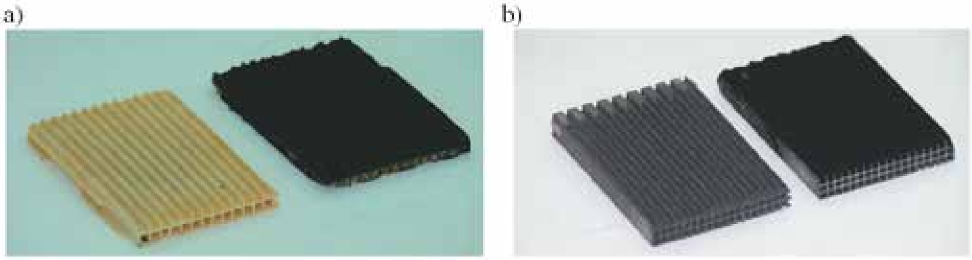

Fig. 2.3. Specimen bases (left) and finished test specimens with model PM layers applied (right): a) specimen base made from cordierite ceramics; b) specimen base made from silicon carbide (SiC) [16]

2.3. Example results of experimental tests

Example time histories of the PM oxidation as recorded during the experiments carried out on the test stand under consideration in identical process conditions have been presented in Fig. 2.4, where Figs. 2.4a and 2.4b show the course of the process with model PM having been applied onto the cordierite ceramic and silicon carbide specimen bases, respectively.

The process conditions were as follows:
- oxidizer temperature T_u = 873 K;
- volumetric oxidizer flow rate $\dot{V}$ = 1 m^3/h;
- molar fraction of oxygen r_{O2} = 21%;
- NO_2 concentration – 50 ppm;
- (model) PM specimen with a mass of about 1 g, prepared from carbon black grade N550 and a small quantity of diesel oil.

In the time histories recorded (Fig. 2.4), the impact of the thermo-physical features of the specimen base on the course of the oxidation process, i.e. on the oxidation duration time and on the shapes of the temperature vs. time curves, can be clearly seen.

Similar time histories, recorded during about 1 000 experiments [1], were used for determining the oxidation kinetics parameter values E_a and k_0 according to the procedure described above. The investigation results revealed strong non-linear dependence of the PM oxidation kinetics on the volumetric oxidizer flow rate $\dot{V}$, the value of which is not directly taken into account in the Arrhenius equation. The investigation also revealed non-linear dependence of the PM oxidation kinetics on the concentration of NO_2 in the oxidizer; the nitrogen dioxide is a gas present in CI engine exhaust gases and it has strong oxidizing properties.

The results of gravimetric measurements carried out in the selected measurement cross-sections of the test system have been described in publications [1] and [6–17]. Within the

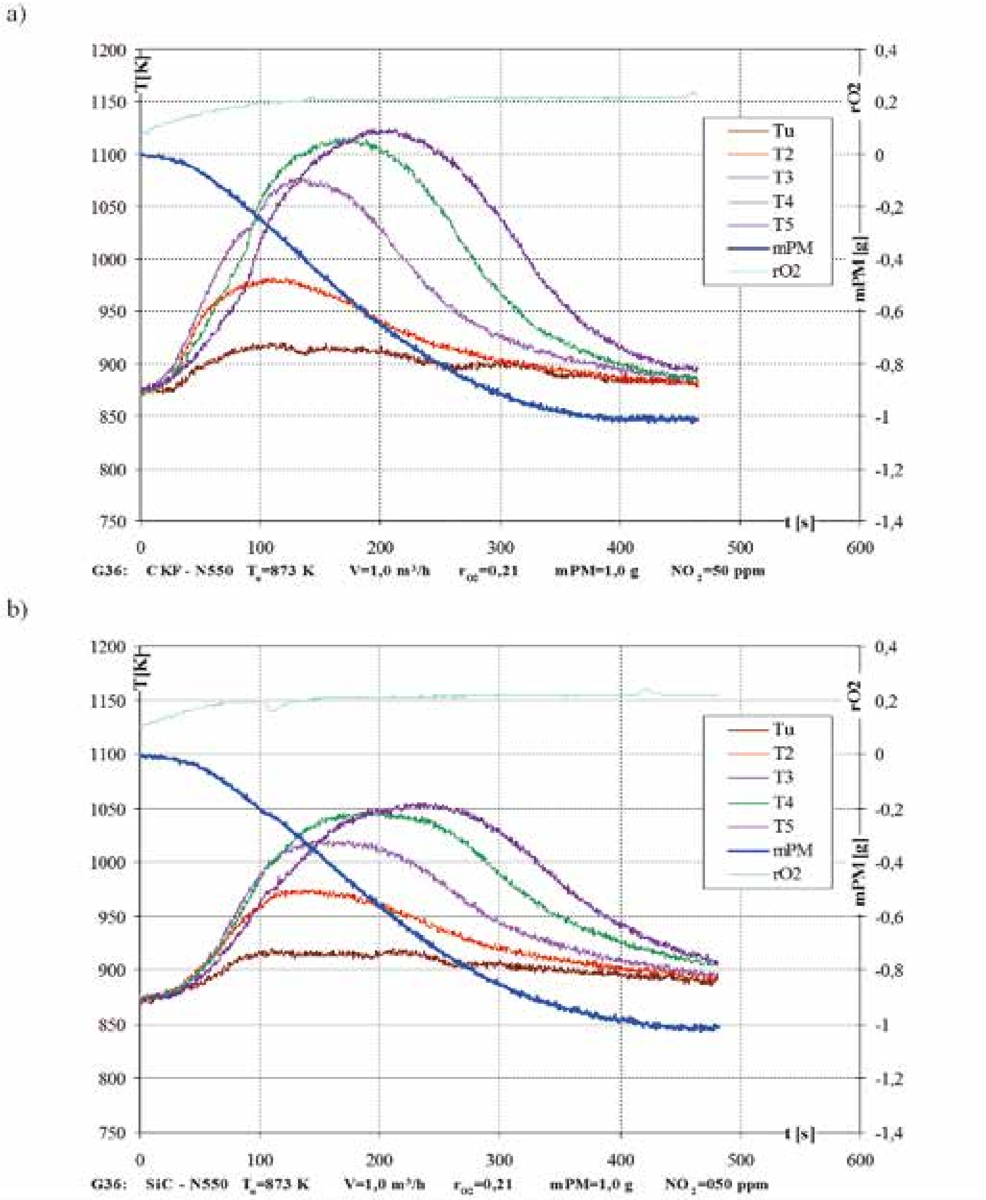

Fig. 2.4. Example time histories of the PM oxidation process, recorded in identical process conditions:
a) for test specimens with bases made from cordierite ceramics;
b) for test specimens with bases made from silicon carbide (SiC) [16]

works described in publications [1] and [16], an attempt was made to analyse the error-generating factors; in result of that analysis, the factors taken into consideration were found not to have any significant impact on the nature of the relationships determined.

Within the work related to the processing and analysing of successive test results, a problem emerged concerning the estimation of the uncertainty of measurement results. The estimation method used, the simplifying assumptions made, and the calculation results obtained with their interpretation have been described in a subsequent part of this paper.

3. Estimation of the uncertainty of measurements with the use of statistical methods

As mentioned previously, the estimation of uncertainty of the quantitative measurements carried out is one of the key factors that make it possible to assess the substantive value of the measurements. The main purpose of estimating the uncertainty of the measurements is to assess their reliability.

On the other hand, elements of estimating the uncertainty of measurements are also required on the international level by normative documents, such as the standard [S1] where organizational and technical requirements for testing laboratories have been laid down. The requirements concerning the estimation of uncertainty of measurements have also been reflected in other recommendations [S2, S3], which often are convergent with requirements of the standard [S1] or define the requirements more precisely. As regards the uncertainty of measurements, testing laboratories are required that, above all, the sources of uncertainty must be identified unless a method exists that would make it possible for the uncertainty to be unambiguously estimated.

In the field of quantitative measurements, there are two groups of the methods to estimate the uncertainty of measurements. One of them consists of the A type methods, which are based on the probability theory, and the other one covers the B type methods, where the probability theory is not used. The A type and B type methods have been more comprehensively discussed in [S2] and [S4].

For the uncertainty of a measurement to be calculated, an A type method must be employed, where the basic and most frequently used tool is the calculus of probability, aimed at determining the mean value of the results of the measurements carried out and the uncertainty interval. For a series of n measurements, where $n > 30$, a classic approach consists in the calculation of a standard deviation of the arithmetic mean and in the application of a selected probability distribution:

$$s_r = \frac{s}{\sqrt{n}} \tag{3.1}$$

where:
n – number of samples;
s – standard deviation of results of a series of measurements, calculated from a formula:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \tag{3.2}$$

where:
x_i – value of the i^{th} sample;
$\overline{x}$ – arithmetic mean value of n samples.

The value of the uncertainty of a measurement result is the product of value s_r obtained from equation (3.1) and a coefficient (denoted by k, according to custom) determined by the confidence level adopted for the assumed probability distribution. The result of such a measurement may be formulated as follows:

$$\mathrm{X} = \overline{x} \pm k \cdot s_r \tag{3.3}$$

If the normal probability distribution is assumed, the value of parameter k may be found in tables of normal probability distribution. In the case of measurements where $n < 30$, the Student's t distribution may be applied instead of the normal distribution.

The decision about the selection of a probability distribution and a confidence level is in every case made by the person who is processing the data. There are cases where the normal distribution cannot be assumed and e.g. a rectangular distribution should be used instead. Moreover, the use of a value other than the arithmetic mean may be reasonable in some cases. As an example, if measurements show that the median value differs from the mean value and tests carried out with the use of a more accurate method show that the measurement result is close to the median rather than the mean, the median value should be adopted as the verified correct value of the measurement result. However, the decision regarding the presentation of the measurement result and estimation of the uncertainty level depends in every case on the person who is processing the measurement data.

In addition to the above, it should be pointed out that the values obtained from the calculations depend on the adopted approach to the data having been collected. As an example, elements of data filtration may be applied to the series of data for the possible outliers to be eliminated. With this end in view, a number of statistical tests have been formulated.

For the purposes of this work, a Dixon's Q test, described e.g. in [18], was used. The use of the Dixon's Q test makes it possible to verify and eliminate bad data from the data set in an easy way. For the Dixon's Q test to be carried out, the data should be arranged in an ascending or descending order. Then, the extreme values are selected and each of them is subjected to the test, where the value of the next sample and the range of data are used for calculations. Depending on the size of the data set, the test is afterwards repeated for the next (nearest) sample or for a sample situated in the series one or two places farther from the sample under test. Such a procedure makes it possible, in large data sets, to avoid a situation where e.g. two successive samples are outliers (i.e. burdened with excessive errors). As an example, if a set of samples is arranged in a series from x_1 to x_n, where $xi \leq x_{i+1}$ and $n > 14$, and the Q-test is applied to sample x_1, then the range of the set is calculated from an equation:

$$\mathrm{R}_{1\to n} = x_{n-2} - x_1 \tag{3.4a}$$

and similarly, for the testing of sample x_n:

$$\mathrm{R}_{n\to 1} = x_n - x_3 \tag{3.4b}$$

In such a situation, the critical values of the test are calculated from formulas:

$$Q_{\min} = \frac{x_3 - x_1}{\mathrm{R}_{1\to n}} \tag{3.5a}$$

and similarly, for sample x_n:

$$Q_{\max} = \frac{x_n - x_{n-2}}{\mathrm{R}_{\mathrm{n}\to 1}} \tag{3.5b}$$

The critical values thus calculated are compared with the values given in the Dixon's test tables, depending on the number n and the confidence level adopted. If the Q parameter values calculated from formulas (3.5) exceed the appropriate value read from the Dixon's test table, then the sample may be rejected as an outlier. The testing according to the procedure as described above may be repeated until all the outliers are eliminated. The Dixon's Q test procedure described in [18] makes it possible to examine this way a set of data consisting of up to 100 samples.

Since the mean value and the standard deviation value do not have to be calculated at the Dixon's Q test, this procedure may be used for a preliminary statistical analysis and verification of measurement results and for the detection of the possible values that might be burdened with excessive errors. The simple Dixon's test, however, is not the only test that would make it possible to reject certain samples as failing to meet specific criteria. In the statistical analysis, there are many tests based on the mean value and the standard deviation value. Unlike the data filtration, which may be carried out on the grounds of specific criteria adopted, statistical tests may help to improve the quality of the results obtained and to increase their accuracy in the context of unambiguous presentation of measurement results.

4. Uncertainty of measurements at gravimetric investigations of parameters of the particulate matter oxidation kinetics

At the investigations of parameters of the particulate matter oxidation kinetics, it was possible to use an A type method with employing the classic method of calculating the mean value and presenting the measurement result in the form of an arithmetic mean value with an uncertainty level calculated on the grounds of the standard deviation of the arithmetic mean for a confidence level adopted.

For the calculations to be made, a set of the data to be subjected to further analysis was selected. The E_a and k_0 parameter values obtained from experiments carried out at an oxidizer temperature of T_u = 873 K were chosen for the basic data set. The decision to use the oxidation kinetics parameters determined for only one temperature point was dictated by the fact that this temperature had a considerable impact on the process and on the values of these parameters. This impact was comprehensively described and subjected to a simulation model analysis in publication [1]. Moreover, the samples were chosen that were obtained from the experiments carried out at volumetric oxidizer flow rates $\dot{V}$ equal to 1 m^3/h and 2 m^3/h and at molar fraction of oxygen r_{O2} = 21% in consideration of small differences in the kinetics parameter values obtained by analysing the measurements carried out in these experiment conditions. An additional argue for the flow rate not to be taken into account was the fact that this quantity is not present in the Arrhenius equation (2.1). Furthermore, a decision was made to select data for the statistical analysis without taking into account the type of the specimen base on which the oxidation process took place. Results of individual measurement results have been brought together at random in Table 4.1. It should be pointed out here that the data presented in the table have the nature of pairs of numbers where each pair was obtained from an analysis of the same experiment; as an example, the values of E_a and k_0 given in item 1 (i.e. for n = 1) are a pair of numbers that have to be taken together at e.g. statistical tests. This means that if the i^{th} value of E_a is rejected in result of a statistical test then the corresponding k_0 value should also be rejected from the data set.

In consideration of the assumptions made at the selection of samples for the basic data set, the data given in Table 4.1 were subjected to a Dixon's Q test according to a procedure briefly described in Chapter 3 herein and in publication [18]. For the test, a confidence level of 95% was assumed as being most often used at analyses of the uncertainty of quantitative measurements. Based on this and for the number of samples in the data set being n = 62, a Q parameter value of the Dixon's test was read from the table provided in publication [18]. The test gave a negative result, i.e. no sample was rejected as an outlier.

Table 4.1. Oxidation kinetics parameters chosen to calculate the uncertainty of measurements

n	1	2	3	4	5	6	7	8	9	10	11	12	13	14
E_a [MJ/(kmolK)]	53.1	50.8	54.5	53.3	51.8	55.4	52.1	51.0	49.6	47.6	45.6	45.1	44.4	48.5
k_0 [1/s]	12.4	10.6	12.2	10.5	11.2	12.9	13.4	10.4	11.5	9.8	12.2	9.8	12.2	14.5
n	15	16	17	18	19	20	21	22	23	24	25	26	27	28
E_a [MJ/(kmolK)]	51.8	50.1	47.8	46.9	45.9	51.9	45.3	54.6	46.8	51.1	48.6	45.2	49.8	47.0
k_0 [1/s]	11.5	12.9	15.5	13.7	5.6	11.6	5.1	13.6	6.1	10.6	8.2	5.1	8.8	6.0
n	29	30	31	32	33	34	35	36	37	38	39	40	41	42
E_a [MJ/(kmolK)]	49.5	48.8	54.3	53.8	49.4	49.0	51.0	51.9	48.8	47.9	52.3	50.2	49.3	49.0
k_0 [1/s]	9.3	8.3	14.3	13.2	14.5	9.3	11.0	12.7	14.1	10.7	19.6	11.1	18.6	13.1
n	43	44	45	46	47	48	49	50	51	52	53	54	55	56
E_a [MJ/(kmolK)]	45.9	47.2	46.6	46.1	51.8	53.6	49.7	51.3	50.1	51.1	49.1	51.4	56.0	51.3
k_0 [1/s]	15.0	14.0	12.9	11.6	15.7	12.1	10.3	11.1	9.3	10.9	8.2	10.9	11.4	12.7
n	57	58	59	60	61	62								
E_a [MJ/(kmolK)]	50.9	52.9	50.3	47.9	48.9	46.6								
k_0 [1/s]	12.2	7.7	18.9	15.8	17.8	11.3								

The set of data as given in the table was used for calculating the mean value of the measurement results, experimental standard deviation (from equation (3.2)), and standard deviation of the arithmetic mean (from equation (3.1)). In addition to this, the values of median and mode of the measurement results were determined. The values obtained from the calculations carried out have been presented in Table 4.2.

Table 4.2. Calculated values of the estimators of measurement results

Parameter	E_a [MJ/(kmolK)]	k_0 [1/s]
Arithmetic mean	49.8	11.7
Median	49.8	11.6
Mode	51.8	12.2
Standard deviation, experimental	2.8	3.1
Standard deviation of the arithmetic mean	0.4	0.4

Based on the calculations made and with assuming the normal distribution of measurement errors for a confidence level of 95%, the overall measurement result could be specified as follows:

$$E_a = 49.8 \pm 0.8 \text{ and } k_0 = 11.7 \pm 0.8$$

An analysis of the uncertainty of measurement results obtained gives grounds for making a statement that for the oxidation rate constant k_0, the uncertainty of the measurement result significantly exceeds the uncertainty of the measurement of the activation energy E_a. This is connected with the fact that the standard deviation of the mean value of the constant k_0 at individual experiments is significant in comparison with the mean value of the constant. The high value of the standard deviation stems from the method of calculation of k_0 from transformed equation (2.3d), where the operation of taking natural logarithm is involved, in consequence of which even a very little change in parameter "b" in formula (2.3d) translates into a significant change in the value of k_0.

The overall measurement results together with results of the measurements carried out during individual experiments have been presented in Fig. 4.1. Individual values of the activation energy E_a measured have been shown as the dark blue points. The mean E_a value has been plotted as the dark blue solid line and the calculated uncertainty interval of the E_a measurement has been indicated by the dotted lines in the same colour. The red points represent results of individual measurements of the oxidation rate constant k_0. The red solid line represents the mean k_0 value, and the red dotted lines indicate the calculated uncertainty interval of the k_0 measurement.

The calculated probability density functions of the normal distributions of values of the oxidation kinetics parameters have been shown in Fig. 4.2. In the same graph, the difference between distributions of the E_a and k_0 values has been visualized. The probability distribution for the k_0 parameter is more uniform, which means that the values of probability that specific measurement result values would occur in the basic data set do not significantly differ from each other. Additionally, the values of the median and mode of the measured parameters of particulate matter oxidation kinetics have been marked in Fig. 4.2. The dotted lines in this graph indicate the intervals of uncertainty of the mean values of individual parameters of the oxidation kinetics.

The kinetics parameters values obtained, presented as the mean values taken from a series of measurements with a measurement uncertainty determined as described previously, are fully acceptable from the point of view of the criteria presented in e.g. [S2] and they may be utilized for further works, e.g. for the works done with the use of simulation models etc.

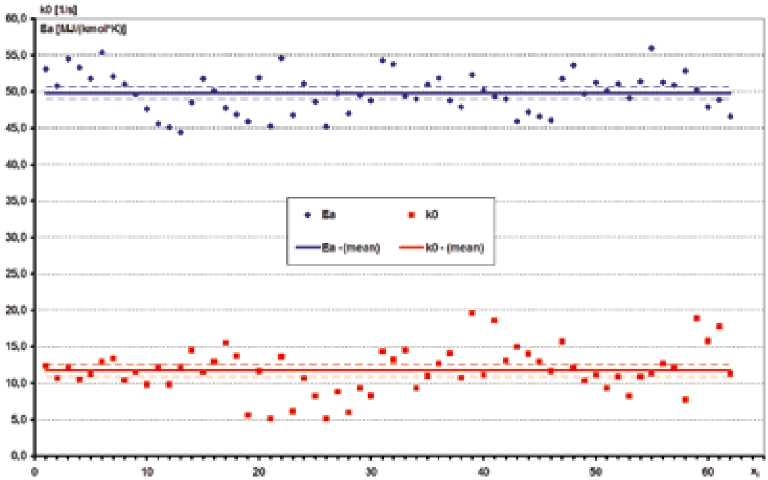

Fig. 4.1. Results of measurements of the kinetics parameters

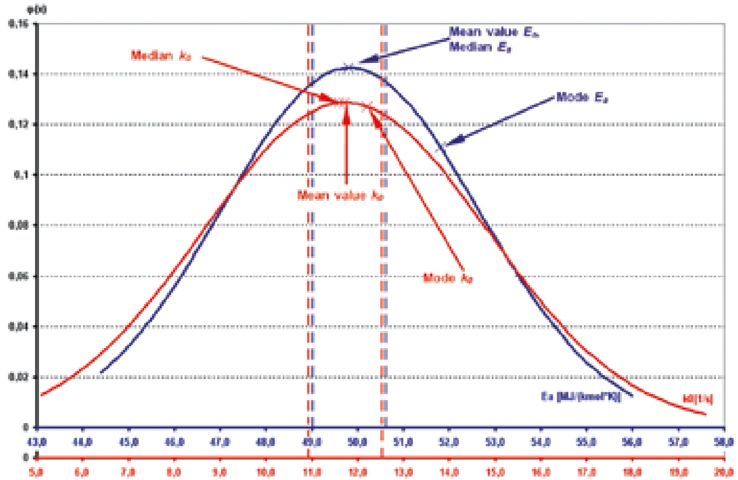

Fig. 4.2. Probability density functions of the PM oxidation kinetics parameters

The results obtained were subjected to verification by calculation, with filtering the measurement results by iteratively eliminating from the data set the results that did not fall within a range defined by multiplying the experimental standard deviation by k (for a confidence level of 95% and the normal probability distribution, $k = 2$). Following the rejection of five pairs of data, the filtering procedure was repeated, which resulted in rejection of another four pairs. The filtering procedure was repeated eight times and a set of 44 pairs of data was obtained in result of that (the rejected pairs of measurement results have been marked by grey filling of cells in Table 4.1). For the said 44 pairs of measurement results, the mean value and standard deviation of the arithmetic mean were calculated again; the calculation results have been presented in Table 4.3.

Table 4.3. Calculated values of the estimators of filtered measurement results

Parameter	E_a [MJ/(kmolK)]	k_0 [1/s]
Arithmetic mean	50.1	11.6
Median	50.1	11.5
Mode	46.6	12.2
Standard deviation, experimental	2.3	1.8
Standard deviation of the arithmetic mean	0.3	0.3

A comparison of the results presented in Tables 4.2 and 4.3 shows that the mean values did not considerably change in result of the filtration as against the unfiltered data. On the other hand, a significant drop (by almost 42% for k_0) can be observed in the experimental standard deviation value. This fact, however, did not translate into a proportional reduction of the standard deviation of the arithmetic mean, which may be explained by a reduction of the size of the data set from $n_1 = 62$ to $n_2 = 44$.

In consequence, the overall measurement result obtained from the filtered data may be presented, like that calculated without filtering the data, in the following form:

$$E_a = 50.1 \pm 0.6 \text{ and } k_0 = 11.6 \pm 0.6$$

To compare the data of the basic population with those of the filtered population, graphs of the probability density function have been plotted for each parameter of the oxidation kinetics.

A comparison of the probability density functions for the E_a values has been presented in Fig. 4.3a. The dark blue and light blue lines represent the probability density functions for the basic data and filtered data, respectively. Similarly, the probability density functions for the k_0 values determined from the basic and filtered data sets have been plotted in Fig. 4.3b as red and green curves, respectively. Fig. 4.3b clearly shows the effect of data filtration. The probability density function for the filtered data is much more concentrated, i.e. the values that are close to the mean value are most likely to occur in the set of the measurement data.

The results calculated in the way as shown from the filtered data also meet the criteria specified in [S2] that concern the estimation of the uncertainty of measurements. The very small differences between the results obtained from the basic and filtered data sets confirm the finding that the results calculated from the basic data set may be considered useful for further research and development works. The results obtained provide also grounds for a statement that the measurement results obtained with the use of the described gravimetric method of investigation of the oxidation kinetics parameters are not burdened with such a degree of uncertainty that the results given in publications [1, 6–17] and their nature might be questioned as untrustworthy.

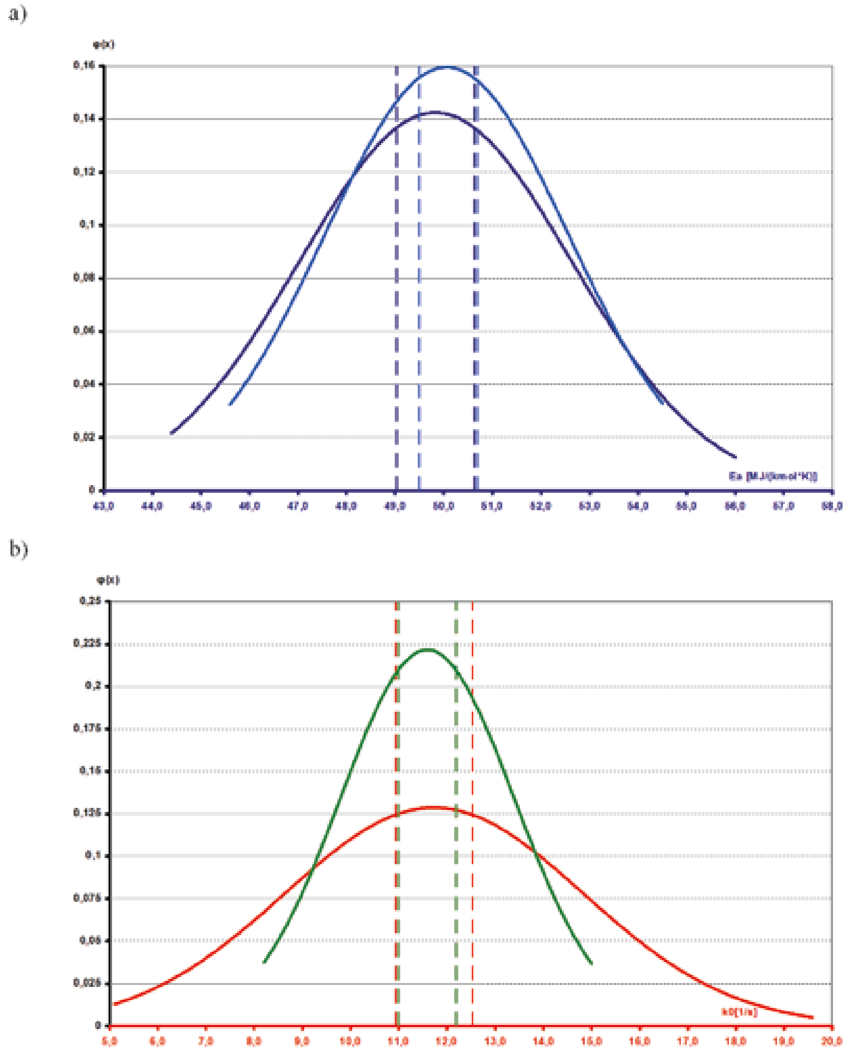

Fig. 4.3. Probability density functions of data of the basic and filtered data set:
a) for the activation energy E_a;
b) for the oxidation rate constant k_0

A statement should be made, however, that although the uncertainty of the results calculated from the filtered population is somewhat lower, such results should not be treated as more accurate, more reliable, or more trustworthy. The reduction of the uncertainty interval was exclusively an effect of the filtration based on rejecting the data that are outside of the range defined by multiplying the experimental standard deviation by k. If another value of the confidence level were chosen, the tendency for reduction in the mistrust interval might be greater, but more samples would be then rejected; hence, the conviction that the measurement results obtained from a smaller population would be more accurate might differ from the reality.

Due to the randomness of the oxidation process and the haphazard nature of the inaccuracies and errors emerging during the measurements, bigger sets of data offer more extensive and more reliable material concerning the substance of the issues analysed. Further works must be carried out to answer the question about the impact of experiment parameters such as volumetric oxidizer flow rate or oxygen content of the oxidizer on the measurement uncertainty value.

5. Recapitulation

This paper presents the effects of estimating the uncertainty of results of determining selected parameters of oxidation kinetics by measurements carried out on a test stand for gravimetric investigation of the kinetics of the PM oxidation process.

The test stand and the test procedure adopted have been briefly described with taking into consideration selected major factors that exert influence on the measurement results. According to previous publications concerning these issues, the factors affecting the measurement results include both the parameters present in the Arrhenius formula and other experiment parameters, which are not taken into account in this formula. Therefore, a need arose to estimate the uncertainty connected with determining the parameters of kinetics of the PM oxidation process.

In this work, an attempt was made to estimate the uncertainty of measurements with the use of statistical methods. The data selected for the analysis were subjected to a statistical Dixon's Q-test, which is to eliminate outliers, and used for calculating the arithmetic mean and the standard deviation of the arithmetic mean. The calculations made it possible to assess the reliability of the determined parameters of PM oxidation kinetics in the defined process conditions. The values having been determined may be useful in experimental and simulation works related to the kinetics of particulate matter oxidation in oxidizer flow conditions, i.e. in conditions similar to those prevailing in automotive exhaust gas filters.

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