



Surface analytical model and sorption artifact designing method

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ABSTRACT

Mass standards with alternative shapes are difficult to design due to the number of complex parameters. An analytical model based on surface sorption experiments is presented to study adsorption. This model is based on an optimization algorithm that is conceptualized to help to design the best sorption artefacts. Experimental artefacts, cylinder-weight and stack-weight, were of the same volume but different surface areas. This algorithm in essence determines the optimum surface of the artefact. After machining the artefact, surface sorption measurements were carried out. A sorption experiment was done by transferring the artefact from air to a vacuum. Then the surface sorption model was set up which represented the relationship between sorption coefficient η , time t and relative humidity h . Logarithmic models were used to fit the variation of sorption coefficient η per relative humidity h with time t .

Section: RESEARCH PAPER

Keywords: mass measurement; surface sorption corrected; mass dissemination; optimization algorithm

Citation: Xiao-ping Ren, Jian Wang, Ombati Wilson, Yong Wang, Bai-fan Chen, Chang-qing Cai, Surface analytical model and sorption artifact designing method, Acta IMEKO, vol. 5, no. 3, article 12, November 2016, identifier: IMEKO-ACTA-05 (2016)-03-12

Section Editor: Marco Tarabini, Politecnico di Milano, Italy

Received December 15, 2015; **In final form** August 1, 2016; **Published** November 2016

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Funding: This work was supported by National Natural Science Funds of China (51405459), National Science and Technology Support Program (2011BAK15B06) and Special-Funded Program on National Key Scientific Instruments and Equipment Development (2012YQ090208).

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1. INTRODUCTION

The unit of mass, the kilogram, is the last of the seven base units of the International System of Units (SI) to be defined according to an invariant of nature rather than a material artefact [1]. Both the watt balance method and Avogadro method are making the new definition under vacuum conditions whereas the current definition of the unit, from the International Prototype Kilogram (IPK), is realized and maintained in air.

After the new definition, it is still necessary to consider traceability from the new realization in vacuum to the current working standards which are always maintained in air [2]. This is to make an indirect link between air and vacuum mass measurements by measuring mass in vacuum and then characterizing the absorption layers of contaminants during the process of transferring from vacuum to air [3]. During this

transition, the mass of the standard is significantly affected by a sorption phenomenon. This phenomenon is caused by atmospheric gases and humidity, which subsequently lead to loss of stability of the mass value of the standard(s) [4]. In 1973, Takayoshi studied the problem of surface water on metal artefacts [5]. R. Schwartz wrote a series of papers on adsorption isotherms in air [6] and sorption phenomena in vacuum [7]. Additional studies focused on Pt/Ir [8], stainless steel [6], [7], silicon [9] and also other materials (Au [8], [10], [11]).

For mass dissemination, there are many parameters to be considered in designing the mass standard, like height, diameter, volume, surface area and mass value of the weight. The characteristics of a measurement instrument are also important such as the size of the mass comparator, electronic weighing capacity and volume measurement instrument. In this paper, an adaptive algorithm which can be used to optimize the design of

a mass standard based on a surface analytic model of mass standards is described.

2. RECENT RESEARCH ON SURFACE ARTIFACTS

One kilogram weights with different surface areas and same nominal mass values are normally required. Samples of different materials (stainless steel, silicon material and platinum-iridium) have to be selected.

Figure 1 shows an example of designing a stack of weights made of platinum-iridium assembled using a spacer (height of 1 cm and diameter of 2 mm). The volumes, masses and surface areas of the spacers were added to the overall values for the weight stack. For some applications of this kind of stack weight, when taking volume measurement, one disc should be placed into the liquid and then the spacer is placed on its surface. Then another disc is put onto the spacer until all the separate discs and spacers are immersed in the volume measurement liquid. During this process, however, the stack of weights may fall down from the magazine and lead to process and system failure.

Another kind of stack weight was composed of a number of discs [6]. These discs were tightened on carrying rods (D : 10 mm). The discs and carrying rods were polished by Häfner Company. For this kind of stack weight, there was a hole in the middle of each disc where the rod was screwed in. These discs cannot be totally seamlessly fixed together (as shown in Figure 2). Thus whenever this stack weight is submerged into the liquid for volume measurement, the volume value would be affected by this gap. A similar design method was described by Beer [13].

Another kind of artefact, shown in Figure 3, consisted of twelve discs separated with pieces of wire and held together with a thin rod. This particular artefact was gold coated with a 6 μm thick layer with an aim of determining the characterizations of the gold surfaces.

In Section 3 we present a mathematical model that, when optimized through computational methods, provides for the best design parameters of the artefacts to be machined.

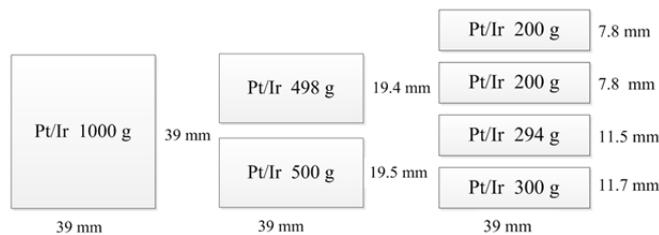


Figure 1. Designing of a platinum-iridium weight set by Johnson Matthey and NPL [12].

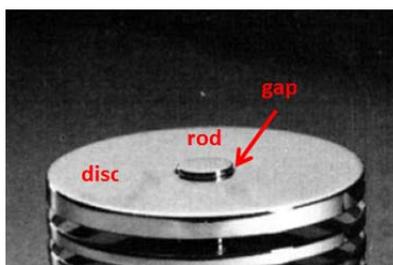


Figure 2. The gap between disc and rod.

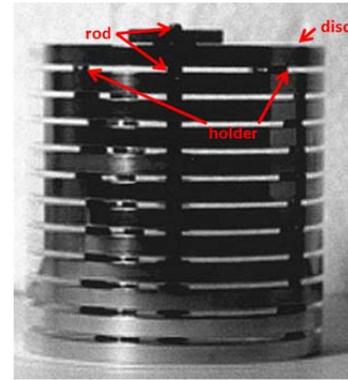


Figure 3. 1 kg gold-plated copper buoyancy artefact.

3. INTEGRAL SORPTION ARTEFACT

In mass measurements, the main uncertainties are due to air buoyancy correction and surface sorption correction. In order to improve the accuracy of the surface analytical model of a mass standard, the most important thing is to reduce the influence of the buoyancy correction as much as possible.

Two prototype models of 1 kg stainless sorption artefacts are shown in Figure 4 and Figure 5. The model represented by Figure 4 is the classical prototype, and it is in cylindrical form with height and diameter being equal. The other model, shown in Figure 5, is in the form of a stack and the discs are separated by a rod. This rod is not however separated from the disc; it is a monolith of stainless steel.

The surface area (S) and volume (V) of a cylinder weight (Figure 4) are shown in (1) and (2), where r , D and H represent the radius, diameter and height of weight respectively.

$$S_{\text{cylinder}} = 2\pi r^2 + 2\pi rH = 2\pi \left(\frac{D}{2}\right)^2 + 2\pi \left(\frac{D}{2}\right)H, \quad (1)$$

$$V_{\text{cylinder}} = \pi \left(\frac{D}{2}\right)^2 H. \quad (2)$$

The dimensions of the stack prototype (shown in Figure 5) are as follows: outer circle's radius and height being R_2 and H_2 respectively; inner circle's radius and height being R_1 and H_1 respectively. The total surface area and volume of 4-level stack prototype are shown in (3) and (4):

$$S_{\text{stack}} = 6\pi R_1 H_1 + 8\pi R_2 H_2 + 8\pi R_2^2 - 6\pi R_1^2, \quad (3)$$

$$V_{\text{stack}} = 3\pi R_1^2 H_1 + 4\pi R_2^2 H_2. \quad (4)$$

Generally, the 4-level stack prototype above is an example of designing the sorption artefact. Different levels can be adopted during design of the sorption artefact depending on the sorption effect. The normal formulae for calculating the volume

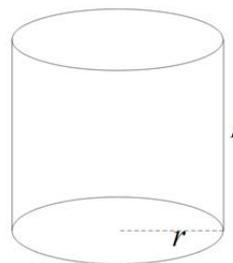


Figure 4. Cylinder prototype.

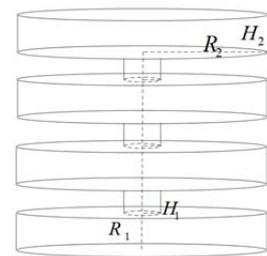


Figure 5. Discs of stack prototype.

and surface area of stack weight with different levels n are shown in (5) and (6):

$$V = (n-1)\pi R_1^2 H_1 + n\pi R_2^2 H_2, \quad (5)$$

$$S = 2(n-1)\pi R_1 H_1 + 2n\pi R_2 H_2 + 2n\pi R_2^2 - 2(n-1)\pi R_1^2. \quad (6)$$

In this research, the two models of mass standards are expected to be of the same volume but different surface areas i.e. (2) and (4) should be equal. Thus, the air buoyancy correction applied during the comparison process will be minimized. The large difference in surface areas between (1) and (3) is better for the mass measurement during transferring from vacuum to ambient.

4. PARAMETER SEARCHING METHOD BASED ON THE OPTIMIZATION ALGORITHM

For the same material with ideal density ρ , and nominal mass value (1 kg), both height H and radius r of cylinder prototype can be calculated by (2). For sorption purposes, let (5) equals the cylinder volume. Thus, there are four parameters which determine the volume of the n -level stack, i.e. R_1 , R_2 , H_1 and H_2 . With surface area of cylinder $S_{cylinder}$ being also known, these four parameters can therefore be varied until the maximum difference between $S_{cylinder}$ and S_{stack} is obtained. However, this design scheme cannot neglect the usage of both mass and volume measurement equipment. All final artefacts therefore can be put into these instruments and their mass and volume can be measured accordingly.

During determining the volume and surface area of the cylindrical prototype, a 9-level stack was considered. This design scheme had the following limitations:

- $R_2 < 50$ mm (size of the weighing magazine);
- height of weight less than 90 mm (volume measurement instrument space);
- volume of 9-level stack equal to the volume of cylindrical prototype i.e. $V_{stack} = V_{cylinder}$;
- surface area of 9-level stack $>$ Surface area of cylindrical weight i.e. $S_{stack} > S_{cylinder}$;
- mass difference between cylindrical and 9-level stack prototype less than or equal to 1.5 g (i.e. electronic weighing capacity). If the mass difference exceeds this limitation, the equipment malfunctions or gives misleading results;
- machining precision equal to 0.01 mm, so the precision of 2 decimal points for each parameter is enough. For example, if the optimal height of the weight H is 53.3725 mm, the value is rounded to 53.37 mm.

In this study, there were six parameters [D , H , R_1 , R_2 , H_1 and H_2] and 6 constraint conditions being considered in the sorption artefact. There are several approaches for solving this kind of multi-object optimization. Matlab has an optimization toolbox with the function "fgoalattain", whose graphical user interface is shown in Figure 6. The following parameters were determined and programmed: start point, goals, weights, linear inequalities, bounds for variables. Objective function and nonlinear constraint function were written into a .m file, which described the formula listed from (1) to (6). More details are given in Appendix I and II.

Start point and final results are respectively shown in Tables 1 and 2. When the optimization algorithm is initially running from the start point, it executes 13 iterations and the algorithm makes the judgement whether volume and surface satisfy the

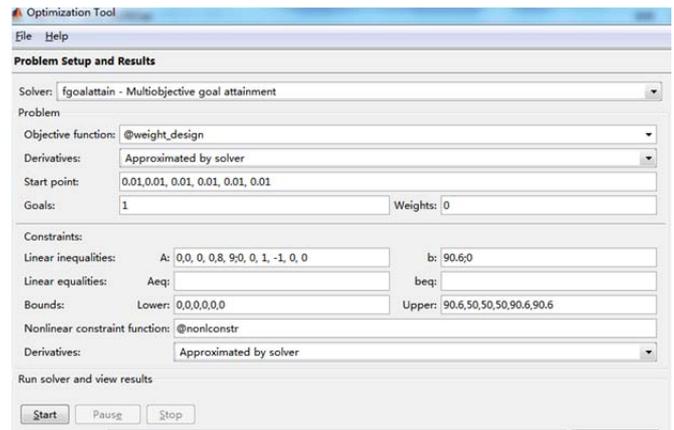


Figure 6. Interface for Global Optimization Toolbox in Matlab 2011.

Table 1. Start Point for the optimization algorithm (unit: mm).

H	R	R_1	R_2	H_1	H_2
0.01	0.01	0.01	0.01	0.01	0.01

Table 2. Optimization result for the start point (unit: mm).

H	R	R_1	R_2	H_1	H_2
53.27	26.64	4.04	50	9.50	1.62

requirement; otherwise, the algorithm is re-executed from the current result until the maximum difference of surface areas is obtained and volume difference is close to zero. Optimization trends of surface area, volume and iteration numbers of optimization algorithm at different start points are shown in Figure 7. Figure 7(b) shows that the optimization sequence of

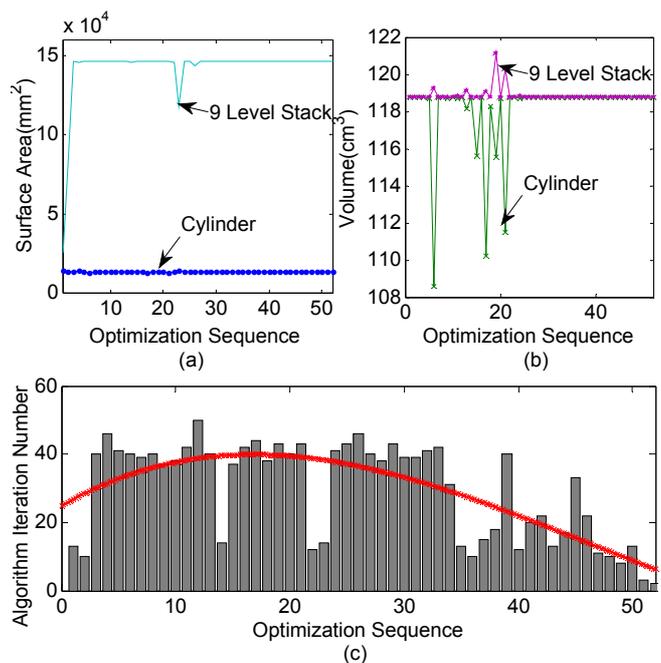


Figure 7. The trend of surface area, volume and the iteration numbers of optimization algorithm at different start points.

volume may have unsatisfactory results (peaks). The curve (red line) in Figure 7(c) represents the variation trends, and shows that the algorithm reached stability after 52 optimization sequences. From this particular optimization results, the maximum surface area difference and volume difference were determined to be 133699.71 mm² and 0 cm³ respectively.

5. SURFACE SORPTION EXPERIMENT

After machining the artefacts (in 2014), their surfaces were thoroughly cleaned (using alcohol) to remove any contaminate e.g. oil and dust. They were subsequently set to stabilize for one year within laboratory ambient condition. These artefacts were also cleaned before the sorption measurements in air and vacuum.

5.1. Surface measurement in air

During this experiment, the masses of the 9-level stack weight and cylindrical weight described in Section 4 were measured using the Mettler-Toledo M-one system. Measurements were performed under normal air condition; their masses were measured from Sept. 10th to Sept. 14th 2015 and the mass differences thereof computed. This measurement procedure was again repeated at the same condition a month later for two days (i.e. Oct. 15th and Oct. 16th). Results of sorption measurements in air are as shown in Figure 8, in which, ΔI , Δm , h , t and ρ respectively represent balance indication, mass difference, relative humidity, temperature in the measurement chamber and air density. The differences between the two series of tests were analysed.

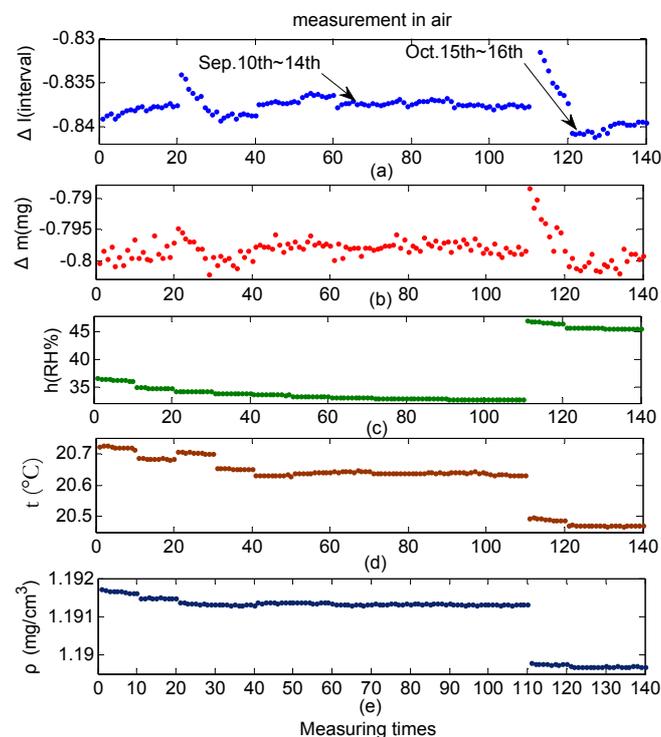


Figure 8. Result of the sorption measurement in air stage
 (a) Variation of the ΔI reading from the balance with measuring times (broken line: long term gap).
 (b) Variation of mass difference Δm with measuring times.
 (c) Variation of relative humidity h with measuring times.
 (d) Variation of temperature t in the measurement chamber with measuring times.
 (e) Variation of air density ρ with measuring times.

5.2. Surface measurement in vacuum

Artefacts were transferred from air to vacuum (TM and PM sensor installed in mass measurement system: M-one); the pressure ranged between 7×10^{-5} Pa and 2×10^{-3} Pa. The sorption was measured from Oct. 20th to Oct. 23th, 2015; results are shown in Figure 9. Figure 9(a) shows that the measurement values were stable at the end of the tests; the last mass difference was -1.2207 mg. Combined with the measurement results in air condition, variation of the relative mass per area A could be determined by mass comparison of the sorption artefacts.

5.3. Relation between sorption coefficient and humidity

In 1994, Schwartz [6] determined the sorption coefficient η as $\eta = \Delta m / \Delta A + \eta_0$. To minimize the effect of η_0 , the current study ensured that the artefacts were thoroughly cleaned before performing measurements, and hence η_0 was assumed to be zero. From the scatter plot of Figure 10, the horizontal axis and vertical axis respectively represent real time t (in hours), and sorption coefficient per relative humidity η/b (unit: $\mu\text{g}/\text{cm}^2/\text{RH} \%$). Sorption coefficient and relative humidity were fit with the aid of the logarithmic model using the following function in (7):

$$f(\eta) = (4.3 \times 10^{-4} + 3.5 \times 10^{-5} \ln(0.43t + 1)) \cdot b. \quad (7)$$

The results obtained from (7) were similar to the results of Schwartz's model of the sorption coefficient. However, unlike Schwartz's model, the present model introduced humidity into the function and also obeyed the logarithmic rule.

This study was congruent with earlier research findings on negligible influence of the effect of roughness condition and temperature of weight surface [6], and did not, therefore, investigate their effects on the sorption behaviour of weight.

6. CONCLUSIONS

In order to provide a practical approach on disseminating the redefined kilogram, realized in vacuum to the mass scale at ambient, processes such as air to vacuum transferring for

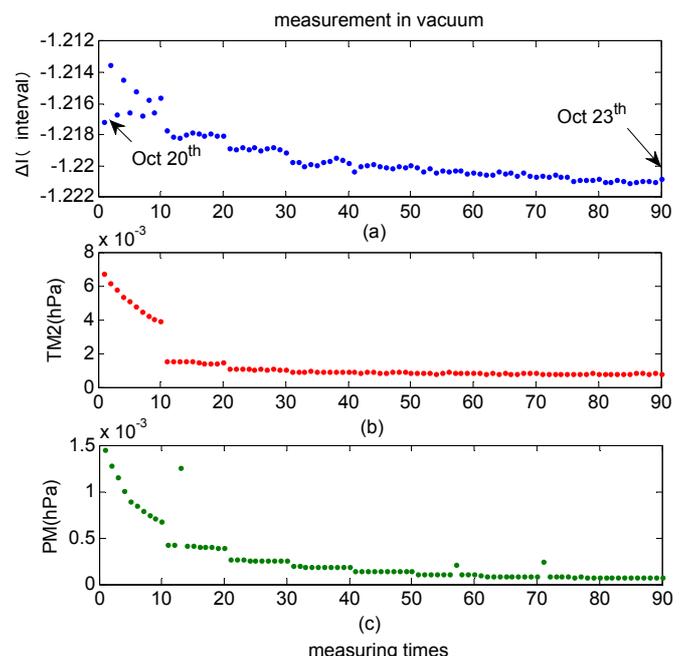


Figure 9. Measuring the mass difference under vacuum condition.

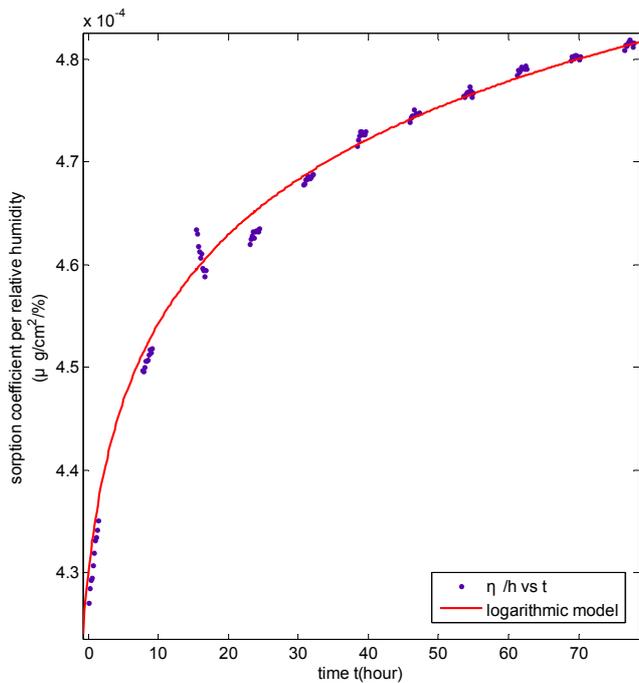


Figure 10. Relation between time t and η/h .

standards must be studied. This transfer process and the results thereof are often affected by adsorption and desorption. In this paper, a new surface analytical model combining artefact standards designing method is presented. The model is based on an optimization algorithm which considers important parameters such as suitable design of weights (i.e. cylindrical weight and stacks of discs of weight). These parameters could help the metrologists in improving the accuracy of mass measurements.

The preparation of the sorption artefact and the sorption measurement has also been described. Sorption coefficient drift was described by a logarithmic function that includes the effects of the humidity and time.

In this experiment, the detailed value of roughness was not given, but the relationship between time, humidity and sorption coefficient was presented. Further research may be conducted in future on artefacts to determine their drift for a long time in air condition.

APPENDIX I

function $f = \text{weight_design}(x)$

density = 8421;

$n = 9$;

$\text{Pi} = 3.14159265$;

$S_{\text{cylinder}} = 2 * \text{Pi} * x(2)^2 + 2 * \text{Pi} * x(2) * x(1)$;

$V_{\text{cylinder}} = \text{Pi} * x(1) * x(2)^2 / 1000$;

$S_{\text{stack}} = 2 * (n-1) * \text{Pi} * x(3) * x(5) + 2 * n * \text{Pi} * x(4) * x(6) + 2 * n * \text{Pi} * x(4)^2 - 2 * (n-1) * \text{Pi} * x(3)^2$;

$V_{\text{stack}} = ((n-1) * \text{Pi} * x(3)^2 * x(5) + n * \text{Pi} * x(4)^2 * x(6)) / 1000$;

$f(1) = -S_{\text{stack}} + S_{\text{cylinder}}$;

APPENDIX II

function $[c, \text{ceq}] = \text{nonlconstr}(x)$

$E1 = 0.5$;

density = 8421;

$n = 9$;

$\text{Pi} = 3.14159265$;

$c(1) = -x(1) * x(2)^2 + (1000 * (1000000 - E1)) / \text{Pi} / \text{density}$;

$c(2) = x(1) * x(2)^2 - (1000 * (1000000 + E1)) / \text{Pi} / \text{density}$;

$c(3) = (1-n) * x(5) * x(3)^2 - n * x(6) * x(4)^2 - (1000 * (E1 - 1000000)) / \text{Pi} / \text{density}$;

$c(4) = (n-1) * x(5) * x(3)^2 + n * x(6) * x(4)^2 - (1000 * (E1 + 1000000)) / \text{Pi} / \text{density}$;

$\text{ceq} = \text{Pi} * x(1) * x(2)^2 - (n-1) * \text{Pi} * x(5) * x(3)^2 - n * \text{Pi} * x(6) * x(4)^2$;

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