

Determination of the Drag-Out

Rolf Jansen and Sigrid Volk

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The consumption of chemicals in processes of surface treatment is mainly caused by the drag-out of bath solution.

Knowing the amount of the drag-out helps to maintain the process stable and is necessary for minimizing waste water and dosage of additives.

Mostly, the values of the drag-out only are estimated - sometimes they are unknown. However, it is very easy to find out how much bath solution is dragged out. This Technical Letter shows how to determine the drag-out using two examples taken from the electroplating technique.

1. Introduction

During surface treatment with process solutions, a film of the bath solution remains on the parts and on the rack/barrel. The bath solution also remains in cavities and gaps, and is transported into the next baths. Due to this transport, the chemicals of the process get lost. The consumption of additives related to the drag-out can be higher than the consumption related to the chemical reaction on the part surface. For instance, the consumption of blue passivation is caused to 90 % by drag-out.

In electroplating processes, especially if high layer thicknesses are deposited, the amount of drag-out is minor to the amount being consumed by electrochemical reaction. Yet, conductivity salts and inert additives are consumed nearly exclusively by drag-out. The amount of drag-out depends on several factors (geometry of the parts and racks, drain times, temperature of the bath solutions, special devices of the plating line) and can differ strongly from one line to another. General values of the drag-out are 20-200 ml/m² for rack application and 100-400 ml/m² for barrel application. But for calculations of the consumption or for instructions of additive dosage these values are indeed too inexact.

2. General Determination of the Drag-Out

2.1. Practical Steps

To measure the amount of drag-out in a processing line, a bath is needed containing ingredients easy to analyse at a high concentration. For example a hydrochloric pickling or a chromium bath are very well suited, since in the following rinse it is easy to analyse the dragged in amount of HCl or chromium.

Procedure:

1. Clean the rinsing bath after the chosen active bath, fill it with fresh water and disconnect it from any circuits.
2. Determine the exact volume of the rinse by measuring width, length, and level.
3. Mix the bath and its rinse well and take a 100 ml sample of each.
4. Run 10-50 racks or barrels through the line, using different parts for representative statistics (count!).
5. Take samples (100 ml) of the rinse in regular periods and analyse them.

If the concentration of the chosen active bath (e.g. pickling, chromium bath) is high enough, for easier calculation it can be considered to have a constant concentration.

2.2. Calculation

Knowing the concentrations of the rinse after different number of racks/barrels, the exact volume of the rinse and the concentrations of rinse and active bath at the beginning, the drag-out can be calculated as follows:

$$V_{d,n} = \frac{C_{r,n} - C_{r,0}}{C_b} \cdot V_r$$

with: $V_{d,n}$ = volume, which is dragged out at rack number n
 $C_{r,n}$ = concentration of the rinse after n racks
 $C_{r,0}$ = concentration of the rinse at the beginning
 C_b = concentration of the bath at the beginning (considered as constant)
 V_r = exact volume of the rinse

Dividing the dragged out volume by the number of racks (n), which have been run through the line, yields in the average volume being dragged out by each rack. If all analysed concentrations are calculated, the average drag-out of this special line can be found out (see the following example).

3 Example 1: Drag-out in a Chromium Line

In a rack plating line of 7200 l chromium electrolyte *SurTec 871* had been an unexpected high consumption of the additive *SurTec 871 II*. The consumption was assumed to be 32 ml per each kg of chromic acid added to the bath. The concentration of *SurTec 871 II* in the bath was not maintained by this addition, leading to faults in the deposited chromium layer, and stock dosages were necessary. The determination of the exact drag-out and the calculation of the consumption based on the drag-out solved this problem.

3.1. Determination of the Drag-Out

To determine the dragged out volume V_d per rack, the rinsing after the chromium bath was prepared freshly and all circuits were disconnected for 35 racks being plated. The concentration of chromic acid in the active bath was 260 g/l and in the rinse it was analysed in regular intervals.

In the following table are listed the concentrations of chromic acid, as well as the cumulated volume of drag-out and the drag-out per rack.

rack	CrO ₃ in g/l	V _A , kum in l	V _A in l/rack
0	0.38		
6	0.67	3.28	0.55
8	0.74	4.07	0.51
10	0.79	4.71	0.47
12	0.85	5.39	0.45
14	0.89	5.87	0.42
16	1.10	8.32	0.52
18	1.16	9.00	0.50
20	1.22	9.61	0.48
22	1.26	10.12	0.46
24	1.39	11.62	0.48
26	1.53	13.23	0.51
28	1.57	13.72	0.49
30	1.62	14.26	0.48
35	1.81	16.51	0.47
chromium bath:	260		

Tab. 1: Drag-out of chromic acid per rack and calculated volume of the drag-out

The concentration of the chromic acid related to the number of racks results approximately in a straight line:

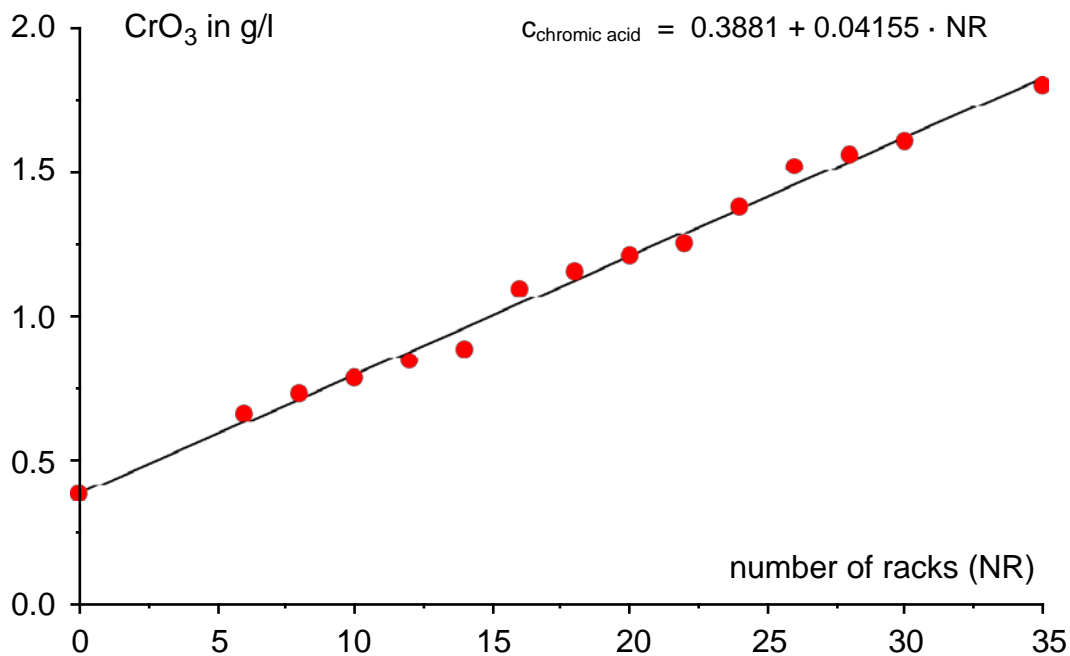


Fig. 1: Dragged out chromic acid related to the number of racks

Because of different types of parts and because of adding chromic acid into the chromium bath, not all of the measured values fit exactly the compensation curve, yet a constant increase of the dragged out chromic acid is obvious.

3.2. Calculation of the Consumption of Additives

The chromium plating line was constructed with a feed-back of rinsing water, and the additive *SurTec 871 II* only is lost by drag-out, and not by the electrochemical reaction.

concentrations of the baths:

chromium bath: 260 g/l CrO₃ and 25 ml/l *SurTec 871 II*

static rinse: 90 g/l CrO₃ and 9 ml/l *SurTec 871 II*

During the plating process an equilibrium state between drag-in and drag-out is formed, thus the concentration in the rinse becomes constant. To determine the consumption of additive *SurTec 871 II*, the following parameters must be calculated, each per rack:

- **Drag-out:**

Using the ascent of the compensation curve above, the known bath volume of the rinse (2800 l) and the concentration of chromic acid in the active bath (260 g/l) the average drag-out volume can be calculated:

$$\frac{0.04155 \text{ g/l} \cdot 2800 \text{ l}}{260 \text{ g/l}} = 0.45 \text{ l}$$

- **Amount of feed-back:**

The feed-back was measured to: 400 l after 1140 racks = 0.35 l/rack

- **Consumption of chromic acid caused by electroplating:**

According to the law of Faraday, the chromic acid consumption can be calculated (with a current density of 25 % (= 0.25), an applied current of 1000 A per rack, a plating time of 4.5 min (= 270 s) per rack, the molar mass of chromic acid of 100 g/mol, a charge transfer of 6 electrons per one chromic acid, the Faraday constant of 96485 As/mol):

$$\frac{0.25 \cdot 1000 \text{ A} \cdot 270 \text{ s/rack} \cdot 100 \text{ g/mol}}{6 \cdot 96485 \text{ As/mol}} = 12 \text{ g/rack}$$

- **Consumption of chromic acid caused by drag-out:**

The amount of chromic acid being dragged out, reduced by the amount of chromic acid being fed back:

$$0.45 \text{ l/rack} \cdot 260 \text{ g/l} - 0.35 \text{ l/rack} \cdot 90 \text{ g/l} = 85 \text{ g/rack}$$

$$\text{total amount of consumed chromic acid: } 12 \text{ g/rack} + 85 \text{ g/rack} = 97 \text{ g/rack}$$

- **SurTec 871 II consumed by drag-out:**

The amount of additive being dragged out reduced by the amount of additive being fed back:

$$0.5 \text{ l/rack} \cdot 25 \text{ ml/l} - 0.35 \text{ l/rack} \cdot 9 \text{ ml/l} = 9 \text{ ml/rack}$$

- **Consumption per kg chromic acid:**

For 97 g CrO₃ 9 ml additive are consumed, thus for 1 kg of chromic acid follows:

$$1 \text{ kg} \cdot 9/97 = \mathbf{92.8 \text{ ml SurTec 871 II}}$$

After calculating the exact amount of drag-out, it was obvious that the estimated value of 32 ml *SurTec 871 II* per kg chromic acid was much too low. Due to this false assumption, the concentration of *SurTec 871 II* decreased steadily below the value being necessary for good plating quality.

4. Example 2: Drag-Out in a Zinc Plating Line

In a rack plating line of 2800 l zinc electrolyte, problems always occurred after a new make-up of the black chromating *SurTec 693*. The old chromating bath (approx. 12 weeks old) was buffered with dissolved zinc (approx. 20 g/l) and at a respective higher concentration of chromium it worked optimal. The freshly prepared black chromating, however, was much more aggressive (needing shorter application times) and it was very sensitive to small variations of the pH-value. As a consequence faults in the passivation layer directly after a new bath make-up occurred frequently.

Even though (being a well-known practice) 350 l of the old chromating bath were used for the new make-up, this artificial working in with 2.5 g/l zinc did not compensate the bath reacting very sensitive.

In order to optimize time and amount of a partly new make-up (to save costs for chemicals and to win process stability), the change of the zinc dissolving rate in the black passivation was calculated as follows. The chromating gets less aggressive when the zinc content rises. However, the zinc concentration does not rise linear, but increases slower towards the end of the service life. In contradiction, the amount of zinc being dragged out grows percental with the zinc content in the solution. Hence, the amount of zinc being dragged out rises to the end of the service life. To calculate the exact change of the zinc content in the black passivation, it is necessary to determine the drag-out firstly.

4.1. Determination of the Drag-Out

In this case, the pickling bath was chosen to determinate the drag-out. It consisted of sulfuric and hydrochloric acid, with a chloride content of 40 g/l. 40 racks were run through the line, at regular intervals 15 samples were taken and the chloride concentration of the samples was analysed. The results as well as the calculated volumes of drag-out are summarised in the following table:

rack	chloride in g/l	V _A , kum in l	V _A in l/rack
0	0.16		
8	0.20	2.32	0.29
10	0.22	4.09	0.41
12	0.24	5.33	0.44
14	0.25	6.15	0.44
16	0.25	6.41	0.40
18	0.26	7.04	0.39
20	0.27	7.73	0.39
22	0.30	9.35	0.43
24	0.31	10.25	0.43
26	0.33	11.53	0.44
28	0.35	12.99	0.46
30	0.37	14.82	0.49
35	0.40	16.94	0.48
40	0.43	18.94	0.47
pickling:	40		

Tab. 2: Drag-out of chloride per rack and the calculated drag-out volumes

The concentration of the chromic acid related to the number of racks, transformed into a graphic drawing, results in almost a straight line.

The linear growing of the dragged out chloride is obvious and the average drag-out volume can be calculated using the ascent of the compensation line:

$$\frac{0.0071 \text{ g/l} \cdot 2800 \text{ l}}{40 \text{ g/l}} = 0.497 \text{ l}$$

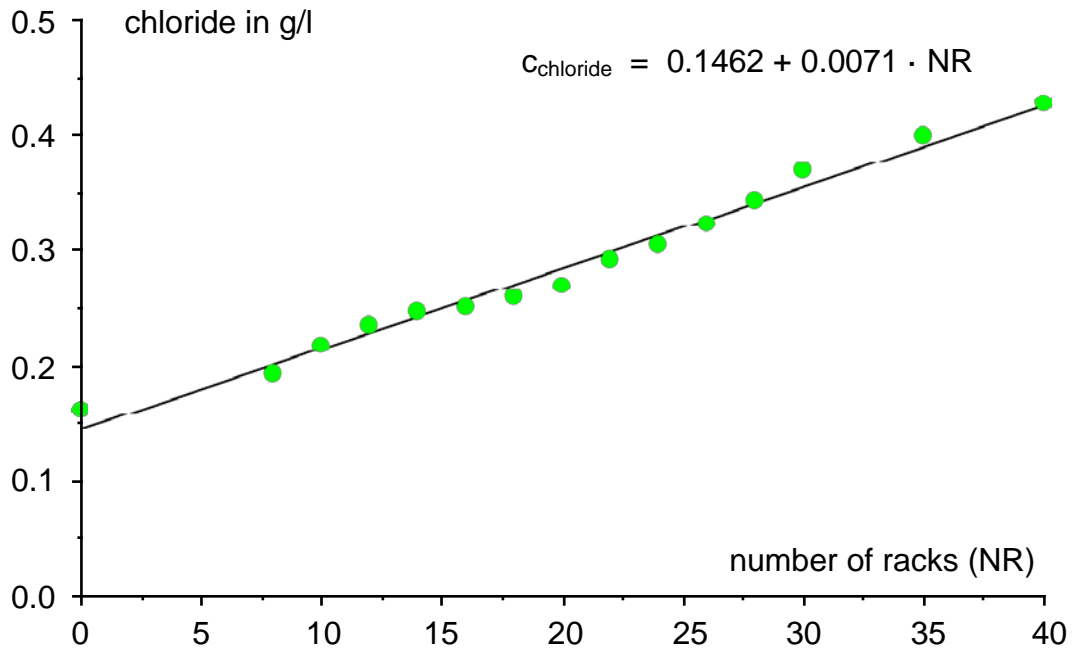


Fig. 2: Dragged out chloride related to the number of racks

4.2 Minimizing the Consumption of the Black Passivation

In order to guarantee the lowest possible consumption of the black passivation *SurTec 693*, it is necessary to know the course of the zinc accumulation in the solution. Then, the best zinc content can be chosen, at which the chromating result is optimal and the increase of the zinc content is the lowest - also including the influence of the drag-out.

The course of the accumulated zinc was observed in a freshly prepared black passivation over a period of 50 working days - which corresponds to 1955 racks:

rack number	zinc content c_{Zn} in g/l
0	0.0
720	10.6
1265	15.3
1471	17.4
1584	18.6
1955	21.0

Tab. 3: Accumulation of zinc in a freshly prepared black passivation over a period of 50 working days

Transformed into a graphic drawing, the result shows not straight a line, but a curve:

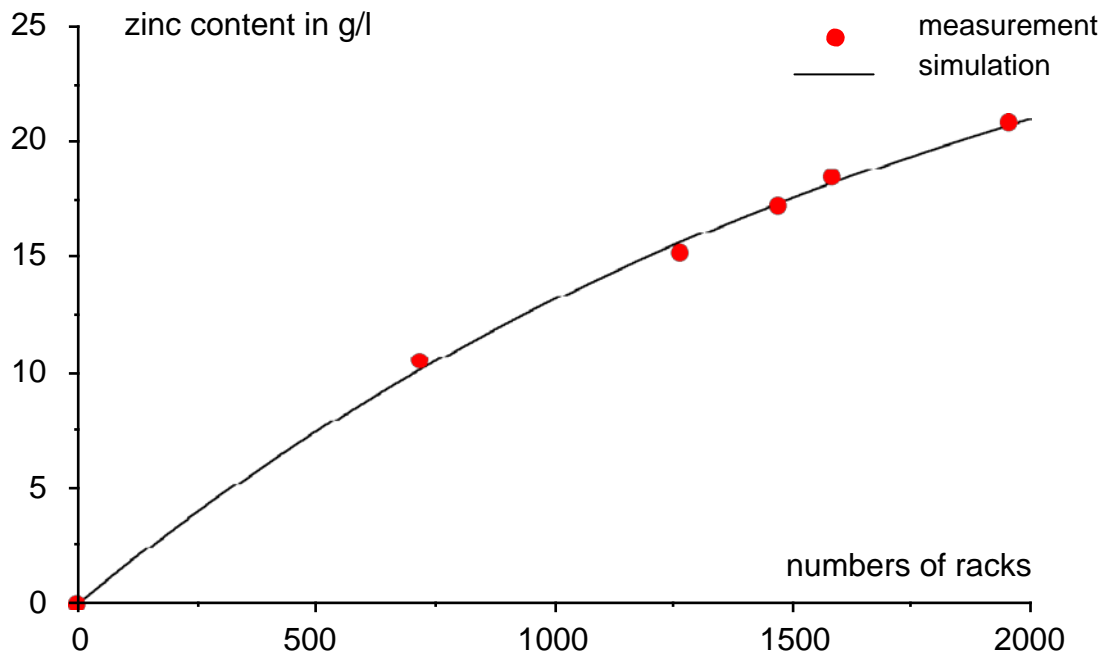
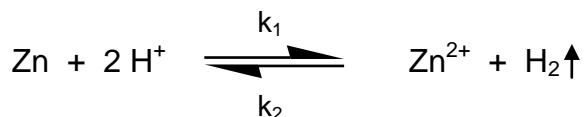


Fig. 3: Increase of the zinc content in a black passivation, the compensation curve is based on a differential formula

The curve is crooked for two reasons:

1) The slower dissolution of zinc due to the high zinc content in solution

This can be explained by the chemical balance of the zinc dissolution reaction: During the chromating process zinc is dissolved due to the attack of acid, and hydrogen is formed:



With increasing zinc content in the bath, the reverse reaction k_2 gets faster. Respectively, k_1 slows down and zinc dissolves less rapid.

2) Higher amount of drag-out in case of higher zinc content in solution

By knowing the calculated drag-out (see the chapter above) of $V_d = 0.497$ l/rack and the bath volume V_b , the dragged out zinc can be calculated as follows:

$$\text{dragged out zinc} = \frac{V_d}{V_b} \cdot c_{\text{Zn}}$$

The formula shows that at rising zinc concentration also the value of drag-out rises.

Both effects slow down the increasing of zinc with the service life of the chromating. The kinetic of the reaction as well as the effect of the drag-out can be described by the following differential equation:

$$\frac{dc_{Zn}}{dt} = k_1 - k_2 \cdot c_{Zn} - \frac{V_d}{V_b} \cdot c_{Zn}$$

with: dc_{Zn} = change of the zinc concentration
 dt = change of the time
 k_1 = reaction constant of the zinc dissolution
 k_2 = reaction constant of the reverse reaction
 c_{Zn} = concentration of zinc in the passivation bath
 V_d = drag-out per time
 V_b = bath volume

By curve fitting of the differential equation to the measured values, following numerical values are derived for the equilibrium constants:

$$k_1 = 0.0171 \text{ g/l} \cdot \text{rack}$$

$$k_2 = 0.000344 / \text{rack}$$

The ascent in each location of the curve shows the increase of the zinc content for each rack. For two values the ascent is calculated as an example via the differential equation:

At 2.5 g/l zinc the ascent (dc/dt) is:

$$\frac{dc}{dt} = 0.0171 \frac{\text{g}}{\text{l} \cdot \text{rack}} - 0.000344 \cdot 1/\text{rack} \cdot 2.5 \text{ g/l} - \frac{0.497 \text{ l/rack}}{2800 \text{ l}} \cdot 2.5 \text{ g/l} = 0.0158 \frac{\text{g}}{\text{l} \cdot \text{rack}}$$

At 20 g/l zinc the ascent (dc/dt) is:

$$\frac{dc}{dt} = 0.0171 \frac{\text{g}}{\text{l} \cdot \text{rack}} - 0.000344 \cdot 1/\text{rack} \cdot 20 \text{ g/l} - \frac{0.497 \text{ l/rack}}{2800 \text{ l}} \cdot 20 \text{ g/l} = 0.00667 \frac{\text{g}}{\text{l} \cdot \text{rack}}$$

Forming the quotient of both ascents, it appears that the zinc content rises 2.4 times faster at an initial content of 2.5 g/l Zn compared to 20 g/l Zn. Hence, a fresh black chromating at a low zinc concentration gets old faster than an old black chromating at a high zinc concentration.

Even compared to the average increase of zinc, formed by the quotient of the total increase of zinc (21 g/l, as in the table above) and the total number of racks (1955, as in the table above):

$$\frac{21 \text{ g/l}}{1955 \text{ rack}} = 0.0107 \frac{\text{g}}{\text{l} \cdot \text{rack}}$$

the dissolution of zinc is $0.0107/0.00667 = 1.6$ times faster than a chromating adjusted at a steady state of 20 g/l zinc.

Respectively, running the black chromating at a zinc concentration of 20 g/l, about 40 % of the chemical consumption can be saved.

The practical transformation into a plating line can be realised by two ways:

1. Small but frequent partly new make-ups

The chromating bath is partially made up new to dilute the zinc content from 21 g/l to 18 g/l (for a bath of 2800 l accordingly 400 l would be made up new weekly).

2. Continuous dosage of chromating concentrate (perfect methode)

A weak steady inflow of fresh (deionised) water and a corresponding discharge of $0.00667 \cdot 2800/20 = 0.93$ l/rack, as well as a dosage of *SurTec 693 A/l*, *SurTec 693 //* and acetic acid, depending on the throughput.

4.3 Calculation of the Diminishing Zinc Layer

Another advantage of working at a constant, high zinc concentration is that the passivation bath is less aggressive. Using the differential equations, the diminished amount of zinc can be calculated, for freshly made up baths (0 g/l Zn) or for older baths (20 g/l Zn), respectively. The subtraction of the drag-out is not allowed now, because the amount of zinc which is dragged out had been dissolved before.

1) Dissolution of zinc at an initial zinc content of 0 g/l

$$\frac{dc}{dt} = 0.0171 \frac{g}{l \cdot rack} - 0.000344 \cdot 1/rack \cdot 0 g/l = 0.0171 \frac{g}{l \cdot rack}$$

Multiplied by the bath volume of 2800 l, the amount of 47.88 g zinc per rack is obtained.

By the aid of the density of zinc (7.14 g/cm^3) and the average surface per rack being plated ($5 \text{ m}^2 = 50.000 \text{ cm}^2$), the diminished zinc in microns can be calculated:

$$\frac{47.88 \text{ g/rack}}{7.14 \text{ g/cm}^3 \cdot 50000 \text{ cm}^2} = 0.000134 \text{ cm} = 1.34 \text{ } \mu\text{m}$$

2) Dissolution of zinc at an initial Zn-content of 20 g/l

$$\frac{dc}{dt} = 0.0171 \frac{g}{l \cdot rack} - 0.000344 \cdot 1/rack \cdot 20 g/l = 0.01022 \frac{g}{l \cdot rack}$$

Multiplied by the bath volume of 2800 l, now the amount of 28.56 g zinc per rack is obtained.

By the aid of the density of zinc and the average surface per rack, the diminished zinc in microns can be calculated:

$$\frac{28.56 \text{ g/rack}}{7.14 \text{ g/cm}^3 \cdot 50000 \text{ cm}^2} = 0.00008 \text{ cm} = 0.8 \text{ }\mu\text{m}$$

That means by using the black chromating at 20 g/l Zn, the zinc maintains thicker and, thus, has a better protection against corrosion.

5. Conclusion

The amount of the drag-out is often unknown or merely estimated. However, sometimes it is responsible for 90 % of the chemical consumption, and it can influence the quality of the plated parts extremely.

As shown in this Technical Letter, it is very easy to determine the drag-out.

The most important steps are summarized below:

- choose a bath with components easy to analyse and at high concentration
- clean the rinsing tank directly after the choosen bath and fill up with fresh water
- determine the exact volume of the rinse by measuring width, length, and level
- stop all additions (concentrates and water) to the bath and its rinse, in particular disconnect both from any circuits
- mix the bath and its rinse well and take a 100 ml sample of each
- run 10-50 racks or barrels through the line, using different parts for representative statistics
- take samples of the rinse regularly and analyse them

With the values obtained by this, the dragged out volume can be calculated.

This "basic knowledge" of the amount of drag-out in a plating line can help in the following to calculate the consumption of additives, to optimize the partly new make-up's, or the dissolution of zinc. Knowing these values will lead to the most wanted result:

Constant good quality of the plated parts!