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Electrochemical applications of net-benefit analysis via Bayesian probabilities

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Abstract By means of three specific applications to electrochemical science, this paper demonstrates the usefulness of the net-benefit principle and Bayesian (posterior) probabilities in deciding whether equipment in an electrochemical laboratory or plant should be repaired or replaced.

Keywords Electrode · Potentiostat · Bayes' theorem · Net-benefit analysis

Nomenclature

B_k	k-th Benefit function
B_{NR}	Net benefit incurred with no repair or replacement
B_R	Net benefit incurred with repair or replacement
C_i	Event of failure caused by the i-th cause
F_j	Event of failure (j = 1) or no failure (j = 2)
$\vec{f}$	Merit – factor vector with elements f_1, f_2,... merits assigned to C_1, C_2,... causes
$P(C_i)$	Unconditional probability of cause C_i
$P\langle C_i \vert F_j\rangle$	Likelihood (conditional probability)of cause C_i when event F_j has occurred
P(F_j)	Prior probability of event F_j
$P\langle F_j \vert C_i\rangle$	Posterior probability of event $F_j$when cause $C_i$has been observed
Φ_i	Merit function carrying appropriate elements of the f– vector
Ψ_i	Merit function carrying appropriate elements of the f– vector

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1 Introduction

Although it may be deemed superficially as a purely business- management technique [1], net – benefit analysis (NBA) based on Bayesian probability theory can also claim science and engineering as its domains of application. Its principle is straightforward: assign a proper benefit parameter to each operating condition, whose posterior probability has been determined by Bayes' theorem, and choose the operation mode which will maximize the net benefit arising from all considered operation modes. It is not imperative to express a benefit in terms of strictly monetary values. If societal, ecological, demographic etc. considerations as well as personal preferences can be combined with technical factors and expressed as scores on an arbitrary scale, net benefits based on such scores can be useful in reaching the right decision.

The prime motivation for this paper is the variety of scenarios electrochemical science and engineering can offer for NBA. Its objective, the illustration of certain (elementary) principles of Bayes' theory applied to electrochemical systems represents a cross-fertilization of two seemingly separate disciplines. By furnishing means to reach past the classical confines of electrochemistry, the paper also indicates what measurements are necessary to utilize fully the predictive nature of probability calculations. In particular, electrode failure, inadmissibly high impurity levels in an electrolyte, drift in measuring and control devices, voltage regulators, premature dysfunction of batteries and fuel-cells are some examples where NBA can be of assistance. The approach, which can be set up at various levels of complexity, has so far received, to the author's knowledge, scant, if any, attention in the electrochemical literature, although certain Bayesian methods have been explored at least in a preliminary manner [2–5].

True to its Bayesian nature, NBA relies to a large extent on the process analyst's personal knowledge and experience related to the physical system under consideration. The symbiosis of ''informed'' subjectivity with objective empiricism is especially manifest in contemporary science of the universe, exemplified by the Yang–Mills theories of the strong and weak nuclear forces which ''feel right'' [6] for partisan physicists.

2 Basic theory

The fundamental structure of NBA, depicted in Fig. 1, is illustrated by the decision procedure where replacement of a process component, or a piece of apparatus in an electrochemical process is to be determined on the basis of failure probability, and the probability of its cause(s). In a single – cause failure, the net benefit may be written as

$$B_R = P(C_1)B_1(\vec{f}) + P(C_2)B_2(\vec{f}) \quad (1)$$

for repair/replacement, and

$$B_{NR} = P(F_1)B_3(\vec{f}) + P(F_2)B_4(\vec{f}) \quad (2)$$

for no action; the benefit parameters B_1 and B_2 are implicit functions of events $F_1$and F_2. They can be further written as

$$B_1(\vec{f}) = P(\langle F_1|C_1\rangle \Phi_1(\vec{f}) + P\langle F_2|C_1\rangle \Phi_2(\vec{f}) \quad (3)$$

and

$$B_2(\vec{f}) = P\langle F_1|C_2\rangle \Psi_1(\vec{f}) + P\langle F_2|C_2\rangle \Psi_2(\vec{f}) \quad (4)$$

where Φ_i and Ψ_i, i = 1, 2 are linear functions of appropriate elements of the merit-parameter f – vector. The posterior probabilities in Eqs. (1) and (2) are provided by Bayes' theorem, discussed briefly in the Appendix, in terms of prior probabilities $P(F_1)$ and $P(F_2)$. The $P\langle C_i|F_j\rangle$ i,j = 1, 2 likelihoods are obtained as

$$P\langle F_2|C_1\rangle = \frac{P\langle C_1|F_2\rangle P(F_2)}{P(C_1)} \quad (5)$$

$$P\langle F_1|C_1\rangle = \frac{P\langle C_1|F_1\rangle P(F_1)}{P(C_1)} \quad (6)$$

$$P\langle F_2|C_2\rangle = \frac{P\langle C_2|F_2\rangle P(F_2)}{P(C_2)} \quad (7)$$

$$P\langle F_1|C_2\rangle = \frac{P\langle C_2|F_1\rangle P(F_1)}{P(C_2)} \quad (8)$$

The unconditional probabilities in Eq. (1) are obtained as

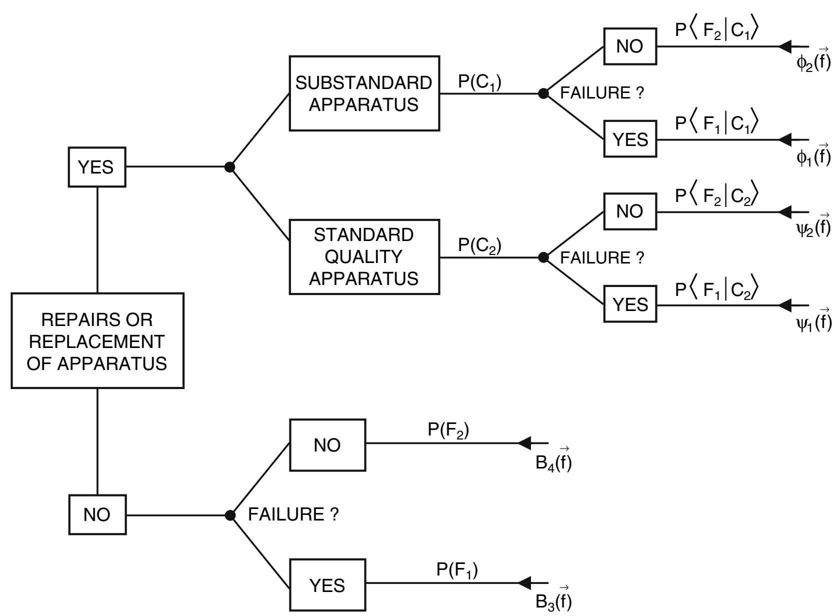

Fig. 1 Flow chart illustrating the NBA approach

$$P(C_1) = P\langle C_1|F_1\rangle P(F_1) + P\langle C_1|F_2\rangle P(F_2) \tag{9}$$

$$P(C_2) = P\langle C_2|F_1\rangle P(F_1) + P\langle C_2|F_2\rangle P(F_2) \tag{10}$$

The symbol $P\langle U|V\rangle$ is the conditional probability that an event U will happen when an event V has already happened. It is the ratio of two probabilities, namely the probability of *both* events U and V occurring, and the probability of single event V occurring, i.e.

$$P\langle U|V\rangle = \frac{P(U\&V)}{P(V)} \tag{11}$$

Since $P(U\&V) = P(V\&U)$, it follows directly from Equation (11) that

$$P\langle V|U\rangle = \frac{P(U\&V)}{P(U)} \tag{12}$$

From a set – theoretical point of view, $(U\&V) = (V\&U)$ are the intersection of sets U and V. If U and V are independent events, then the conditional probabilities are simply the product of the single – event probabilities $P(U)P(V) = P(V)P(U)$.

The process analyst can follow essentially two paths to obtain probabilities. Collecting information from plant and laboratory reports, consulting with experts of the subject area, inferring from related scientific, engineering and statistical literature are major steps in the first path. The second path, involving the execution of appropriate experimental protocols under the analyst's guidance/direction, may necessitate more effort and expenditure than the first ‘‘external’’ path, but it may be more reliable, especially if external data are only partially available.

An important corollary of Eqs. (11) and (12), that a conditional probability can be high even if its constituent probabilities are low, is illustrated by a hypothetical failure of five out of one thousand identical batteries after 90% of their rated ampere – hour capacity has been exhausted (event V), and electrolyte leakage from three such batteries (event U) accompanying the failure. Here, $P(V) = 0.005$, and $P(U\&V) = 0.003$ are very low, but the probability that a battery will leak if it is known that it has failed: $P\langle U|V\rangle = 0.003/0.005 = 0.6$ is much higher.

The benefit components are assigned scores within a specific interval according to the analyst's scheme of assessment. This is the essentially subjective part of NBA, but subjectivity is an integral part of the Bayesian approach, with its virtues and limitations discussed amply in pertinent literature; a particularly lucid critique is given by Balmer [7].

3 Application to electrochemical processes

3.1 An introductory problem: simplified analysis of electrode failure

Three possible causes C_1, C_2, C_3 of electrode failure, called event F, in a process are assumed. C_1 denotes substandard material and fabrication; C_2 poor hydrodynamic conditions (e.g. the existence of undesirable stagnation zones in the cell); C_3 improper maintenance. On account of recent improvements in the fabrication process, the process analyst assigns relatively low prior probabilities $P(C_1) = 0.18$ and $P(C_2) = 0.27$, but recognizing the continued existence of maintenance problems, the relatively high $P(C_3) = 0.55$. Likelihoods) $P\langle F|C_1\rangle = 0.3158$; $P\langle F|C_2\rangle = 0.1842$; $P\langle F|C_3\rangle = 0.5000$ are established on the basis of a set of observations shown in Table 1. The unconditional probability of failure is computed as

$$P(F) = (0.31585)(0.18) + (0.1842)(0.27) + (0.5000)(0.55) = 0.8288 \tag{13}$$

The posterior probabilities are, in consequence, $P\langle C_1|F\rangle = (0.3158)(0.18)/0.8288 = 0.0685$; $P\langle C_2|F\rangle = (0.1842)(0.27)/0.8288 = 0.0600$; $P\langle C_3|F\rangle = (0.5000)(0.55)/0.8288 = 0.3318$. If the analyst assigns merit parameters 5, 7, 9 to causes C_1, C_2, C_3, respectively, on a scale of zero (best) to ten (worst), then improper maintenance is deemed to be the most ‘‘costly’’ [(0.3318)(9) = 2.99] cause of electrode failure, followed by poor hydrodynamics [(0.0600)(7)] = 0.42, and substandard material/fabrication [(0.0685)(5) = 0.34]. This order is not unique; another analyst with a different set of merit parameters in mind may well draw different conclusions.

Table 1 Establishment of likelihoods in the simplified analysis of electrode failure (Sect. 3.1)

Observation period P_i	Number of electrode failures ascribed to causes C_1, C_2, C_3		
	C_1: faulty fabrication	C_2: hydrodynamics	C_3: poor maintenance
P_1	7	4	3
P_2	4	3	7
P_3	5	3	9
P_4	5	2	6
P_5	3	2	8
Totals	24	14	38
Per cent	31.58	18.42	50.00
$P\langle F\|C_i\rangle$	0.3158	0.1842	0.5000

3.2 NBA of a malfunctioning electrode

This is a more involved variation of the theme in Sect. 3.1, using a somewhat different orientation to decide if a certain electrode should be repaired or replaced. F_1 denotes the event of electrode failure, F_2 denotes the complementary event of no electrode failure, C_1 is the event that the electrode is of substandard quality, and C_2 is the complementary event that the electrode is of acceptable (standard) quality. Considering that electrode failure might occur even with an electrode of acceptable quality, and that even a substandard electrode might not necessarily fail, the following merit parameters are defined: f_1 for acceptable electrode performance; f_2 for electrode replacement; f_3 for operating with a substandard but so far not failed electrode; f_4 for failure of a substandard electrode; f_5 for failure of a standard – quality electrode during operation. The associated merit functions are $\Phi_1 = (f_2 + f_3 + f_4)$; $\Phi_2 = (f_2 + f_3 – f_1)$;$\Psi_1 = (f_2 + f_5)$; $\Psi_2 = (f_2 – f_1)$, and $B_3 = f_4$; $B_4 = –f_1$. A 2% prior failure rate of electrodes is postulated; likelihoods $P\langle C_1|F_1\rangle = 0.95$; $P\langle C_1|F_2\rangle = 0.002$; $P\langle C_2|F_1\rangle = 0.05$; $P\langle C_2|F_2\rangle = 0.998$ are postulated in the manner of Sect. 3.1 . Since $P(F_1) = 0.02$ and $P(F_2) = 0.98$, the unconditional probabilities $P(C_1) = 0.02096$; $P(C_2) = 0.97904$; and posterior probabilities $P\langle F_1|C_1\rangle = 0.9065$; $P\langle F_1|C_2\rangle = 0.00102$; $P\langle F_2|C_1\rangle = 0.09351$; $P\langle F_2|C_2\rangle = 0.99898$ are computed in accordance with Sect. 2. It follows that Eqs. (1) and (2) yield net benefit $B_R = 0.02096B_1 + 0.97904B_2$ for repair/replacement, and $B_{NR} = 0.02B_3 + 0.98B_4$ for no action.

Table 2 presents four decision patterns with arbitrary magnitudes of the merit factors. In the shown arrangement, the less positive (more negative) are the values of B_R and B_{NR}, the more desirable is the pertaining decision. This is an arbitrary, but consistent scheme (its converse would be equally consistent and admissible). The first three cases are similar in the sense that assigned ''penalty'' for electrode failure is high, while operation with a substandard electrode which has not yet failed is judged to deserve small penalty. In all three cases the indicated decision would be not to replace nor to repair the electrode. In the fourth case, the benefit of working with an acceptably performing electrode is assigned a high score, while other factors are deemed to have a low value. Although $B_R$is technically larger than B_{NR}, they are sufficiently close to support either decision.

Table 2 The effect of merit factor magnitudes on decision in Sect. 3.2; scale for f – vector elements: 0 (worst) – 10 (best)

	Case 1	Case 2	Case 3	Case 4
f_1	4	3	1	8
f_2	5	5	3	1
f_3	2	2	2	1
f_4	7	9	10	3
f_5	6	7	10	3
B_1	12.972	14.878	13.972	3.971
B_2	1.261	2.280	2.011	–6.989
B_3	7	9	10	3
B_4	–4	–3	–1	–8
B_R	1.261	2.280	2.760	–6.769
B_{NR}	–3.78	–2.76	–0.78	–7.78
Indicated decision	NR	NR	NR	NR?

3.3 NBA analysis of an electroanalytical potentiostat

In this illustration, occasional drifting of a potentiostat placed between the waveform generator and the cell in an impedance – measuring apparatus [8] is considered. The potentiostat is assumed to possess a high-quality drift sensor with a 98.2% probability of sensing a true drift, and a 0.5% probability of sensing falsely a non – occurring drift. The prior probability of drifting is 1%. Merit factor $f_1 = 30$ is assigned to the sensing of a true drift, f_2= 5 to repair of the potentiostat; $f_3 = 10$ to false sensing; $f_4 = 15$ to not sensing a true drift and $f_5 = 3$ to ignoring the existing (salvage) value of the potentiostat. It follows that $\Phi_1 = (f_2 – f_1) = –25$; $\Phi_2 = (f_2 + f_3 + f_5) = 18$; $\Psi_1 = (f_2 + f_4) = 20$; $\Psi_2 = (f_2 + f_5) = 8$. In addition, the analyst is assumed to penalize a no – repair/no replacement decision by merit factor f_6 for not taking advantage of current availability of funds (these funds may be accessible only for a limited length of time).

Table 3 summarizes the computations required for decision. At low f_6 values the right decision is no action, inasmuch as $B_{NR} < B_R$. At large values of f_6 repair or replacement is favoured, due to the high degree of merit assigned to it.

4 Discussion

The foregoing analysis can readily be extended to multiple-cause decision processes so long as the required likelihoods are known. In Sect. 3.2, e.g., electrode failure may also be due to inefficient maintenance (event C_3), with related likelihoods $P_3|F_1\rangle$ and $P\langle C_3|F_2\rangle$ and posterior probabilities $P\langle F_1|C_3\rangle$ and $P\langle F_2|C_3\rangle$. The f – vector is appropriately augmented with merit factors assigned to C_3 – related occurrences

Table 3 Summary of calculations for Sect. 3.3

Events: D_1: drift; D_2: no drift; S_1: sensing of drift; S_2: no sensing of drift
Prior probabilities: $P(D_1) = 0.01$; $P(D_2) = 0.99$
Likelihoods: $P\langle S_1 \vert D_1\rangle = 0.982$; $P\langle S_2 \vert D_1\rangle = 0.018$; $P\langle S_1 \vert D_2\rangle = 0.005$; $P\langle S_2 \vert D_2\rangle = 0.995$
Unconditional probabilities:
$P(S_1) = P\langle S_1 \vert D_1\rangle P(D_1) + P\langle S_1 \vert D_2\rangle P(D_2) = 0.01477$
$P(S_2) = P\langle S_2 \vert D_1\rangle P(D_1) + P\langle S_2 \vert D_2\rangle P(D_2) = 0.98523$
Posterior probabilities: $P\langle D_1 \vert S_1\rangle = P_1 \vert D_1\rangle P(D_1)/P(S_1) = 0.6649$
$P\langle D_1 \vert S_2\rangle = P\langle S_2 \vert D_1\rangle P(D_1)/P(S_2) = 0.000183$
$P\langle D_2 \vert S_1\rangle = P\langle S_1 \vert D_2\rangle P(D_2)/P(S_1) = 0.33514$
$P\langle D_2 \vert S_2\rangle = P\langle S_2 \vert D_2\rangle P(D_2)/P(S_2) = 0.9998$
$B_1 = P\langle D_1 \vert S_1\rangle\ (f_2 - f_1) + P\langle D_2 \vert S_1\rangle\ (f_2 + f_3 + f_5) = -10.5907$
$B_2 = P\langle D_1 \vert S_2\rangle\ (f_2 + f_4) + P\langle D_2 \vert S_2\rangle\ (f_2 + f_5) = 8.00205$
$B_3 = f_4 + f_6 = 15 + f_6$
$B_4 = f_6$
$B_R = P(S_1)B_1 + P(S_2)B_2 = 7.7274$
$B_{NR} = P(D_1)B_3 + P(D_2)B_4 = 0.15 + f_6$
Decision: if $f_6 < f_6^* = 7.58$; no repair or replacement
if $f_6 > f_6^*$; repair or replacement (f_6^*: crossover point)

(when the C – event set is large, techniques of linear algebra can be particularly useful for computation). Similarly, repair and replacement may be assigned different f – values instead of a lumped treatment.

Merit can also be expressed in terms of actual costs, i.e. by assigning appropriate monetary units (MU). If real cost values are employed, the degree of subjectivity may arguably be smaller, but two or more analysts may not necessarily agree, however, on a specific MU – cost associated with any element of the f– vector.

The advantages and drawbacks of the Bayesian approach having been amply discussed in the literature, including references cited in this paper, their discussion is omitted here. It is instructive to point out, nevertheless, one fundamental divergence from (classical) non – Bayesian theory: population parameters (e.g. mean and variance) are considered to be random quantities, instead of deterministic constants. In this framework, the updating of prior probabilities and likelihoods is especially as important for a realistic application of Bayesian techniques as the availability of a sufficiently large data base.

5 Final remarks

The still limited understanding and appreciation of the power of probabilistic/statistical concepts by many scientists has recently been pointed out in a thoughtful albeit provocative article written by a senior soil scientist [9]. Whether electrochemical science fares at present better than its sister disciplines is a matter of conjecture. In any event, there is still a long way to go in utilizing probability theory and statistical analysis to their full extent. The current paper is intended to be a modest step in this direction.

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6 Appendix

6.1 A brief illustration of Bayes' theorem

For the sake of simplicity two mutually independent events: $A_1$and $B_1$with their complements A_2 and B_2 are considered; $P(A_1) + P(A_2) = 1$, and $P(B_1) + P(B_2) = 1$. Bayes' theorem yields the conditional probabilities of events A_1 and A_2 occurring given that events $B_1$and B_2, respectively, have occurred. As shown by Equations (A.1) and (A.2), they depend on previously established A_i; $i = 1,2$ – driven probabilities as

$$P\langle A_1|B_1\rangle = \frac{P\langle B_1|A_1\rangle P(A_1)}{P\langle B_1|A_1\rangle P(A_1) + P\langle B_1|A_2\rangle P(A_2)} \quad (A.1)$$

and

$$P\langle A_2|B_2\rangle = \frac{P\langle B_2|A_2\rangle P(A_2)}{P\langle B_2|A_1\rangle P(A_1) + P\langle B_2|A_2\rangle P(A_2)} \quad (A.2)$$

with $P\langle A_2|B_1\rangle = 1 - P\langle A_1|B_1\rangle$, and $P\langle A_1|B_2\rangle = 1 - P\langle A_2|B_2\rangle$ serving as shortcuts in lieu of further two equations similar to Equations (A.1) and (A.2). Proofs based on set – theoretic interpretations of probability can be found in a large variety of textbooks on probability and statistics.

A commercial potassium-ion selective electrode with a valinomycin membrane (active material $[(C_{10}H_{21}0)_2PO_2^-]$ and 1 μmol dm^{-3} – 1 mol dm^{-3} range [10] serves for illustration. Major interferers with accurate indication are cesium and ammonium ions. The theorem applied to four events considered in Table 4 indicates a very high reliability of the instrument in the absence of the interfering species $[P\langle A_2|B_2\rangle \approx 99.9\%]$, but only a moderate reliability in their presence $[P\langle A_1|B_1\rangle \approx 75.2\%]$. The very low conditional probabilities $P\langle B_2|A_1\rangle$ and $P\langle A_1|B_2\rangle$ support, however, the candidacy of this instrument for field use.

Table 4 Computations required by Bayes' theorem (Appendix). Events: A_1: interfering species (IS) present in the sample; A_2: IS absent from the sample; B_1: incorrect indication of potassium-ion content in sample; B_2: correct indication of potassium-ion content in sample CIPIC: correct indication of potassium-ion content; IIPIC: incorrect indication of potassium-ion content

Event probability	Interpretation	Calculation via Bayes' theorem (*)	Equation
$P(A_1) = 0.03$	3% of all samples contain IS	Postulated	N/A
$P\langle B_1\vert A_1\rangle = 0.98$	98% chance of IIPIC with IS in sample	Postulated	N/A
$P\langle B_1\vert A_2\rangle = 0.01$	1% chance of IIPIC without IS in sample	Postulated	N/A
$P(A_2) = 0.97$	97% of all samples do not contain IS	$1 - P(A_1)$	N/A
$P\langle B_2\vert A_1\rangle = 0.02$	2% chance of CIPIC if IS are present	$1 - P\langle B_1\vert A_1\rangle$	N/A
$P\langle B_2\vert A_2\rangle = 0.99$	99% chance of CIPIC if IS are absent	$1 - P\langle B_1\vert A_2\rangle$	N/A
$P\langle A_1\vert B_1\rangle = 0.752$	75.2% chance that IS are present in case of IIPIC	$\frac{(0.98)(0.03)}{(0.98)(0.03)+(0.01)(0.97)}$	(A.1)
$P\langle A_2\vert B_1\rangle = 0.248$	24.8% chance that IS are absent in case of IIPIC	$1 - 0.752$, or $\frac{(0.01)(0.97)}{(0.01)(0.97)+(0.98)(0.03)}$	Version of (A.1)
$P\langle A_1\vert B_2\rangle \approx 0$	Near zero chance that IS are present in case of CIPIC	$\frac{(0.02)(0.03)}{(0.02)(0.03)+(0.99)(0.97)}$	Version of (A.2)
$P\langle A_2\vert B_2\rangle \approx 1$	Near 100% chance that IS are absent in case of CIPIC	$1 - P\langle A_1\vert B_2\rangle$ or $\frac{(0.99)(0.97)}{(0.99)(0.97)+(0.02)(0.03)}$	(A.2)
$P(B_1) = 0.0391$	3.91% chance of IIPIC	$(0.98)(0.03)+(0.01)(0.97)$	N/A
$P(B_2) = 0.9609$	96.1% chance of CIPIC	$1 - P(B_1)$ or $(0.99)(0.97)+(0.02)(0.03)$	N/A

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