

Analytical Method to Monitor Industrial Pickling Baths Initially Constituted by HF, HNO₃

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Abstract

The present study couples the acid/basis titration and the ICP analysis in order to monitor the concentrations of nitric and hydrofluoric acids, and presents into baths used to pickle alloys of titanium or stainless steel, largely employed in the aeronautic industry. The pickling of the alloys releases various metallic cations able to react with HF in order to lead to metal-fluoride complexes and free H⁺, the last being able to react with the basis. In this study, it was determined: the most significant correlations providing the number of the protons released by the complexation of the metallic cation by the fluoride. The proposed method based on: 1) these correlations; 2) the titration pH = f(V_{KOH}) curves; and 3) the content of metallic cations determined by ICP, enables the monitoring of the content of HNO₃ and HF into the pickling bath. Assuming that one bath was used for one type of alloy (alloys of Titanium for example, or alloys of stainless steel), then the proposed method appears providing reliable concentration values of both acids as well as metallic cations.

Keywords

Pickling Bath Monitoring, Mix HF/HNO₃ Titration, Fluoride-Metallic Cations Complexation, Titanium Alloys Pickling, Stainless Steel Alloys Pickling

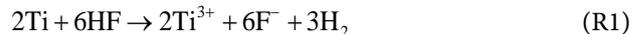
1. Introduction, Objectives of the Study—Brief Bibliography

The aeronautic industry uses various alloys of stainless steel, or titanium to manufacture aircraft's elements, typical compositions of which were indicated in **Table 1**.

The elaborated elements must be pickled before their surface conditioning or treatment [1] and various type of bath were involved. The commonly used pickling solution are aqueous mixtures containing HNO₃ (3 to 6 M) and HF (0.5 to 2

M) ([2] [3] [4] [5]), which could also be used to pick other metals such as silicon [6]. Several studies deal with the oxidation of these alloys and various reactions were proposed for the oxidation of their constituting metals.

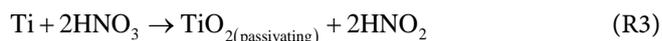
Concerning titanium alloys pickled by HF alone, studies achieved by Sutter [3] [5], conclude that oxidation takes place according to the reaction (R1):



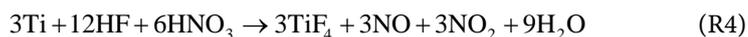
Then, oxidation of Ti^{3+} by the atmospheric oxygen occurs, leading to $\text{Ti}^{(\text{IV})}$ complexed by the fluoride ions in excess. Say [4] proposes a similar attack reaction for the pickling of the alloy TB (Table 1), by HF (R2). Nevertheless, attack by HF alone is not recommended because of the hydrogen embrittlement of the alloy:



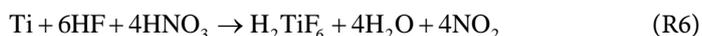
In general, pickling was not performed using nitric acid alone because it releases passivated oxides or others products which cause the pickling to be stopped:



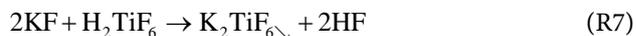
To avoid passivation or hydrogen embrittlement, several authors suggest to pickl using the mixture HF/ HNO_3 . For titanium alloys, Tongwen [7] proposes the reaction (R4) followed by the side reaction (R5) which releases H_2TiF_6 :



However bibliography also reveals the simpler reaction (R6):



Note that H_2TiF_6 is assumed to be a strong di-acid, able 1) to dissociate to $\text{TiF}_6^{2-} + 2\text{H}^+$ and 2) to give various equilibria leading TiF_4 , TiF_5^- , or TiF_6^{2-} as function of the hydrofluoric acid concentration. Moreover, its corresponding salt (K_2TiF_6) appears to be solid in aqueous media as claimed by Mecaprotec company [8], which processes to the pickling bath regeneration by addition of KF according to the reaction (R7):



Similar reactions and also complexes between iron and fluoride occur during the pickling of stainless steel alloys by HF/ HNO_3 bath. Hermoso *et al.* [9] study the recovery of iron and chromium from pickling baths by precipitation, keeping nickel in solution. Authors report on obtained crystals of K_2FeF_5 and CrF_3 , with a little fraction of other oxides and fluorides phases at $60^\circ\text{C} - 65^\circ\text{C}$, pH 4.1 - 4.2.

Galvez *et al.* [10] claim that fluoride-metal complexes with high stabilization constants appear during the pickling of stainless steels by HF/ HNO_3 bath. They propose a model of the various equilibria involving 25 reactions and 31 species, and conclude that FeF_3 , CrF^{2+} and Ni^{2+} are the main metallic forms in the solu-

tion.

The rate of the pickling and the state of the surface of the alloys after treatment are strongly conditioned by the acids concentrations ratio that is why this ratio must be monitored. Empirical operations are often employed to know if it is required to replace the bath: typically optical observation of the state of the surface of the element (after pickling) often constitutes the criterion. Furthermore, the pickling rate determined on metallic-calibrated-specimens constitutes also another criterion. Besides, studies carried out by Sutter [3] on the titanium pick in HNO₃/HF bath show that the pickling rate strongly decreases for [HF]/[Ti] < 5.4 and the bath becomes inoperative for [HF]/[Ti] < 1.9. The authors claim that the oxidation leads to TiF_n⁽ⁿ⁻⁴⁾⁻, a specie able to be hydrolyzed to oxygenated complexes releasing HF, according to (R8):



The bibliography shows various sophisticated analytical techniques which claim the monitoring of the concentrations of a mixture of HF and HNO₃. Raman (Kang *et al.* [11]) and near infrared [12] spectroscopic evaluations were proposed to detect mix of HNO₃/HF. However, the real selectivity and reliability of all these methods, established using model solutions, must be proved with real industrial samples, especially long life time baths susceptible to contains various metallic ions.

Acid-base titration by potentiometric detection (e.g. pH=f(V_{titrating agent})) is a simple and low cost and technicality analytical method, which is used by the sub-contracting operators of the aircraft industry, for the surface treatment, in order to monitor the content of acids (HF and HNO₃) in the pickling baths; however potentiometric curves were not always correctly resolute; moreover, some subcontractors (in our geographic area) report that titration of industrial baths provides erroneous results and lacks in the reliability. Typically, metallic cations produced by oxidation of the alloys, can complex with fluoride or precipitate with the hydroxide ion of the titrating basis and cause drastic errors on the determined concentration of the acids.

Coupled to the alkalimetric titration, Lindroos [13] proposes to determine the concentration of the free HF in the pickling bath by direct potentiometry (E_{(V)/SCE} = a + log[F⁻]) using a fluoride-selective electrode; however authors mentions not explained interferences with the bridge of the reference electrode. Other authors [5] [8] [10] [14] achieve confrontation of the experimental titration curves to the corresponding simulated curves (obtained assuming various complexation equilibria). Titrations of 12 synthetic pickling liquors achieved with potassium hydroxide, seems providing good agreement and low errors in concentration prediction [10]. Mean relative error claimed for metal concentrations is 0.4% for iron and nickel and 1.4% for chromium; while the mean relative error for anions is 4% for fluoride and 1% for nitrate. Authors claim that 1) sodium hydroxide cannot be used as titration agent [10], as sodium-fluoride ion interaction displaces equilibrium and makes singular points of titration curves to overlap; and

2) the dissolved chromium only marginally affects the HF concentration. Note that the selectivity all these additional technics must be validated with real industrial bath and that is the main remaining problem to be solved.

The objective of this study is to propose a new method enabling reliable monitoring of the contents of both HNO₃/HF acids into a real industrial bath.

First titration of simple mixture of HNO₃/HF acids will be performed in order to select the appropriated media and titrating agent. Then, the effect of metallic ions (released from the alloys), on the titrating basis volume and also on the shape of the pH-metric curve will be examined, according to two separated cases: 1) metallic ions arise from titanium alloys; and 2) ions arise from stainless steel alloys; the aim is to determine the possible interferences as well as the corresponding equations. Finally ICP measurements of the metallic ions contents into industrial baths will be performed in order to validate the proposed method.

2. Experimental Devices, Methods and Chemicals Used

Studied alloys of titanium and steel

The compositions (mass contents) of various types of titanium and stainless steel alloys, susceptible to be pickled, are presented in **Table 1**. All the metallic components are susceptible to be present into the used pickling baths under ionic form complexed or not with fluoride ions.

All chemicals were normapur products supplied by Sigma-Aldrich, and the experiments were achieved at room temperature ($18 < T(^{\circ}\text{C}) < 22$).

Acid-base titrations were achieved using the Metrohm automatic titrator "Toledo 888". The pH was monitored using a combined glass electrode specific of the H⁺. When the titration was carried out in organic solvent, the pH probe used is an LL-solvotrode, immersed in LiCl saturated ethanol. For titrations performed in water, an *Ecotrode Plus from Metrohm (membrane glass type KCl= 3 mol/L, Internal reference electrode type Ag/AgCl/KCl saturated water)*, was used.

The titrating agent volume at the neutralization, was read at the inflexion point of the pH=f(volume) curve (simple and derivative). Between each titration, in order to remove possible deposit from both glass membrane and porous ceramic of the reference electrode, the probe has been cleaned with demineralized water and then by the appropriated solvent. For baths with high contents in cations, at the end of the titration, due to large quantity of deposit, the electrode has been immersed in water under agitation during 10' and then stored in LiCl electrolyte (in the appropriated solvent). To have an operative electrode, its calibration procedure must be performed, using standard rules and provider's recommendations. Due to the possible damages of the electrode by HF and/or by solid deposits, the calibration step must be regularly performed (as a function of the titrations number, between 1 calibration per day and 1 per week).

Titration of the cationic species contained into the alloys were achieved by

Table 1. Contents of titanium and stainless steel alloys used in the aeronautic industry and examined in the present study. Values provided by the suppliers and checked by ICP.

Alloy abbreviated name	Metallic specie (mass percent)											
	Ti	V	Al	Mo	Zr	Nb	Sn	Cr	Fe	Ni	Cu	Others
TA	~99											<1
TB	~89	~4	~6									<1
TC	~79	~5	~5	~5	<1.5	<1.5		~3				<1
TD	~85		~6	~2	~4		~2					<1
IA								17 to 19	60 to 70	10 to 20		
IB								14 to 15	70 to 78	4 to 6	2.5 to 4.5	

Table 2. Acid-Base information concerning the species contained in the pickling baths involved in the present study.

Species	Solvent				Remarks
	Water	Ethanol	Acetone		
HF	3.1	5.0	~5.5		Acidity decrease in organic solvents
HNO ₃	-1.0	-1.0	~ -1		Strong acid in the examined solvents
Metallic cations arising from alloys indicated in Table 1.	*In absence of complexing ligands, all the cations could react with bases for pH ranges from 2 to 8. *The acidic behavior of the cations is strongly dependent 1) of their complexation, mainly by the fluoride ion, and 2) by the media used.				

inductive coupling plasma. (ICP-OES, ULTIMA 2-HORIBA, nebulizer chamber in Teflon).

3. Results and Discussion

3.1. Selection of the Appropriated Basis and Solvent for the Titration of the Mixture of HNO₃/HF

The industrial pickling bath contains initially HNO₃/HF at various concentrations; we choose pickling baths containing initially these acids under the following concentrations: $3 < \text{HNO}_{3(\text{M})} < 5$ and $0.5 < \text{HF}_{(\text{M})} < 1.5$.

Various species could be used as titrating basis: NaOH, KOH, tetrabutyl-ammonium hydroxide/TBAOH, amines. To avoid toxicity risks, the amine type bases will not be considered. KOH, NaOH and Tetrabutyl ammonium hydroxide (TBAOH)) were examined here in order to select the more appropriated. Each one exhibit advantages and drawbacks; for example, solubility in soda (aqueous or not) of the metallic cations is lower compared to the other bases and the produced solid species causes the fouling of the combined pH electrode. In a similar way various solvents were available to carry out the titrations (**Table 2**); as a function of the pK of the acid in the solvent the titration curve can be well resolute or not.

In order to have a nice separation of the volumes required to neutralize two different acids, the difference between the pK of these acids must be at the least two units. **Table 2** provides the pK of HF and HNO₃ in various solvents, and

clearly shows that, for the HF titration, it is better to operate in ethanol (or acetone) than in water ($pK_{\text{ethanol}} > pK_{\text{water}}$).

However, whatever the media, the presence of metallic cations (complexed or not) is able to disturb the neutralization curve in the same pH range, because: 1) hydroxides of these metallic cations could precipitate and 2) these cations, complexe with fluoride and could lead to some strong acids neutralized simultaneously.

In order to select both the solvent and the basis, each acid was titrated separately and then the titration of their mixture (e.g. the pickling bath) was performed. In the light of the obtained results (curves $\text{pH} = f(V_{\text{basis}})$, **Figure 1**) titration using aqueous solution of soda (**Figure 1(a)**) was rejected, because the low resolution of the curve obtained with the mixture of both acids. This curve does not enable the determination of both concentrations separately.

The same titrations were performed using KOH (**Figure 1(b)**) or TBAOH (**Figure 1(c)**) into ethanol, and the obtained curves exhibit nicely resolute waves for each acid, consequently both KOH and TBAOH, in ethanol, could be selected to pursue analyses. According to the **Table 2**, acetone is the solvent expected to provides the best results because the highest pK differences ($pK_{\text{acetone-HF}} - pK_{\text{water-HF}} = 2.4$).

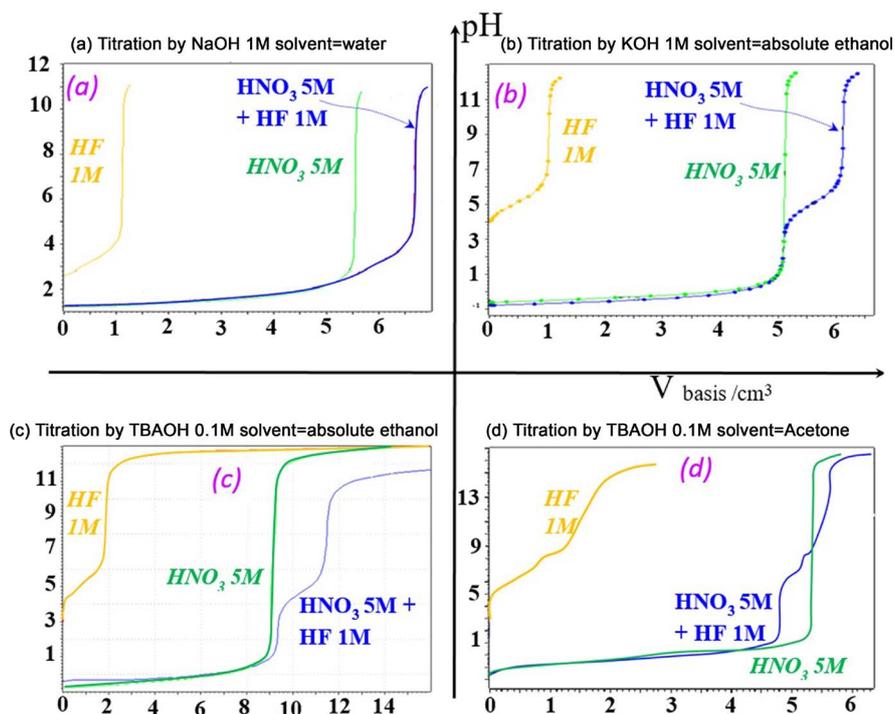


Figure 1. Titration, by various bases and in various solvents, of the acids HNO_3 /HF alone or in mixture. Metrohm Toledo 888 titrator, solvotrode, room temperature, agitation. For titrations by KOH or NaOH ((a), (b)): Quantity of the solution to be analyzed: 1 mL; Final volume of the mixture to be titrated: 50 mL (completed using the selected solvent); For titrations by Tetrabutyl ammonium hydroxide (TBAOH ((c), (d)): Quantity of the solution to be analyzed: 0.2 mL; Final volume of the mixture to be titrated: 50 mL (completed using the selected solvent).

However, titration of HF using acetone (**Figure 1(d)**) leads to a curve containing two “low resolution” waves, meaning a decomposition or some complexation/reaction leading to two different acids (HF, HF_2^- , or some other adducts). Consequently, the use of acetone will be excluded.

To sum up both KOH and TBAOH bases in ethanol solvent enables separated determination of the concentrations of the acids used in the pickling baths. In absence of interfering species, the first neutralization (V_{e1}) is attributed to the nitric acid, while the second one (net volume = $V_{e2} - V_{e1}$, where V_{e2} is the total volume measured) represents the reaction with HF.

3.2. Influence of Some Species Produced by the Pickling of the Alloys on the Neutralization Volumes ($\text{pH} = f(V_{\text{basis}})$)

This section examine the effect of the concentration of the most abundant elements of the alloys (susceptible to be oxidized during the alloy pickling), on the neutralization waves of both HF and HNO_3 acids. It is expected to get a better understanding of the phenomena taking place in order to propose the more reliable method enabling the monitoring of the contents of the HNO_3 and HF acids into industrial pickling baths. In order to simplify the investigation we consider in this study baths containing both HF and HNO_3 acids, used to pickle alloys of: 1) titanium; and 2) stainless steel.

3.2.1. Alloys of Titanium

1) Influence of the titanium concentration (under the form H_2TiF_6) on the acid-base titrations of a mixture of acids HNO_3 , HF

The titanium is the main metal ($80 \leq \text{mass percent} \leq 99$) constitutes the titanium alloys; its cations, especially $\text{Ti}^{(\text{IV})}$, are able to forms acidic compounds by complexation with the fluoride anions [3] [7] [8]. This section expects to study the plausible reaction of these species by the previous selected bases (KOH and TBAOH in the ethanol solvent) and to determine possible interferences on the waves of the neutralization of HNO_3 and HF.

The **Figure 2** exhibits the curves obtained by titration of mixtures of HNO_3 5 M, HF 1 M and H_2TiF_6 , at three different concentrations, within ethanol by respectively two titrating bases: top/(i): KOH 1 mol/L; and bottom/(ii): TBAOH 0.1 mol/L. The curves clearly indicate a different behavior of the H_2TiF_6 acid against the titrating basis.

For titrations carried out by KOH (**Figure 2(i)**), the obtained $\text{pH} = f(V_{\text{KOH}})$ curve contains two neutralization waves, whatever the concentration of the H_2TiF_6 ; increasing this last from 0.2 to 0.6 M cause the volume of the first neutralization (attributed to HNO_3) to increase, confirming that the H_2TiF_6 is a strong acid, neutralized simultaneously to the HNO_3 . The second part of the curve in **Figure 2(i)**, *i.e.* the second wave (previously attributed to the neutralization of the HF), is just shifted to the right, but the corresponding volume remains constant.

In order to determine the protons number of the H_2TiF_6 neutralized (during

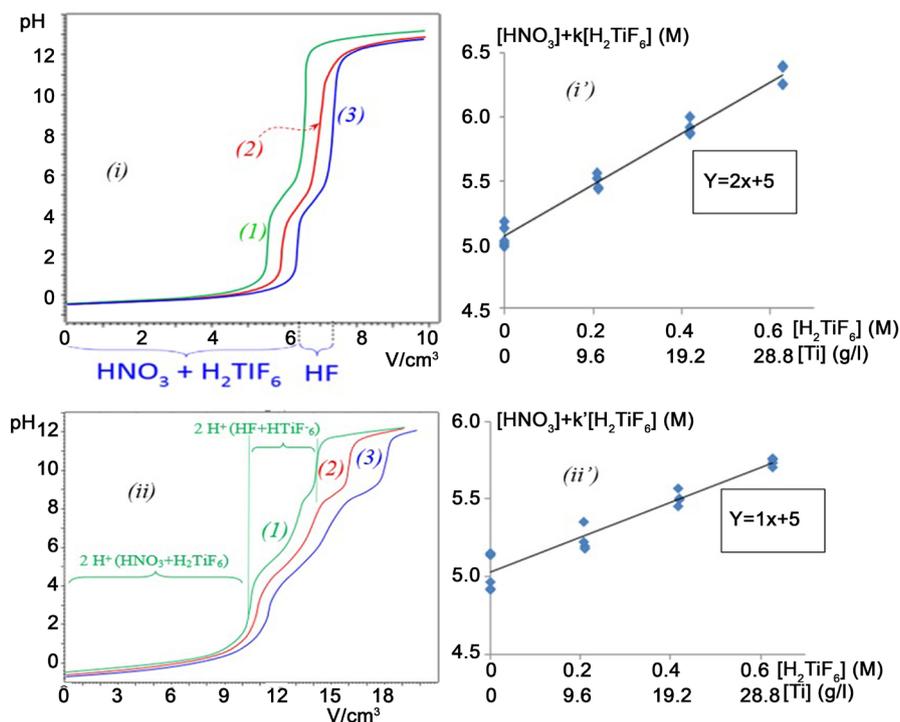


Figure 2. Titration curves of the mixture HNO₃ 5 M, HF 1 M and H₂TiF₆ at three different concentrations, by two titrating bases (left-top (i): KOH 1 mol/L; and left-bottom (ii): TBAOH 0.1 mol/L) in the absolute ethanol. H₂TiF₆ concentration: 0.21, 0.42 and 0.63 M for respectively curves (1) green, (2) red and (3) blue curve. Room temperature, agitation, Metrohm Toledo 888 titrator, solvotrode. Left-top (i): Quantity of the solution to be analyzed: 1 mL; Final volume of the mixture to be titrated: 50 mL (into ethanol). Right-top (i'): Evolution of the total acidity (deduced from the volume of the first neutralization (curve i, 1) as a function of the added known-concentration of H₂TiF₆ into the mixture containing HNO₃ 5 M/HF 1 M (several solutions have been tested). Left-bottom (ii): Quantity of the solution to be analyzed: 0.2 mL; Final volume of the mixture to be titrated: 50 mL (into ethanol). Right-bottom (ii'): Evolution of the total acidity (deduced from the volume of the first neutralization (curve ii, 1) as a function of the added known-concentration of H₂TiF₆ into an initial mixture containing HNO₃ 5 M and HF 1 M (several solutions have been tested).

the first wave of the curve), the total acidity (deduced from the first neutralization) was plotted against the H₂TiF₆ “added” concentration in the mixture of HF/HNO₃ (Figure 2(i’), experiments triplicates).

A straight line, deduced from the first neutralization, describes the evolution of the total acidity against the added concentration of the H₂TiF₆ (e1):

$$([\text{HNO}_3] + k \times [\text{H}_2\text{TiF}_6]) = 5.07 + 2.0 \times [\text{H}_2\text{TiF}_6]; R^2 = 0.98 \quad (\text{e1})$$

The observed slope is equal to 2, meaning that the H₂TiF₆ releases “two protons” which are neutralized during the first acid-base reaction; in these conditions, it behaves as a strong di-acid, neutralized in the same pH range as nitric acid (HNO₃ × 1H⁺ and H₂TiF₆ × 2H⁺). In absence of another interfering species, the volume of the second neutralization (second wave) can be used to determine the hydrofluoric acid concentration.

Different results were obtained when titrations were carried out by TBAOH. The $\text{pH} = f(V_{\text{TBAOH}})$ curves (**Figure 2(ii)**) contain three neutralization waves (instead two for the titration with KOH). Increasing the concentration of the H_2TiF_6 from 0.2 to 0.6 M appears to affect the volume of the three neutralizations. As previously, analysis of the evolution of the first neutralization wave versus the added concentration of the H_2TiF_6 was achieved and the results were reported in **Figure 2(ii')**; a straight line describes the evolution of the total acidity against the added $[\text{H}_2\text{TiF}_6]$ and it obeys to Equation (e2):

$$([\text{HNO}_3] + k' \times [\text{H}_2\text{TiF}_6]) = 5.03 + 1.1 \times [\text{H}_2\text{TiF}_6]; R^2 = 0.93 \quad (\text{e2})$$

The observed slope, very close to 1, means that one proton of the H_2TiF_6 reacts with TBAOH, simultaneously to the HNO_3 , during the first neutralization. H_2TiF_6 behaves in these conditions, as a strong mono-acid.

Comparison of the curves (i) and (ii) in **Figure 2** enables to conclude that the salt K_2TiF_6 (solid as claimed by Mecaprotec company [8]) is more stable than the $(\text{TBA})_2\text{TiF}_6$. Concerning the second and the third neutralization-waves of the curves (**Figure 2(ii)**), it is not obvious to attribute them to the HF or $(\text{TBA})_1(\text{H})_1\text{TiF}_6$; indeed, both volumes increase when the concentration of the added H_2TiF_6 increase from 0.2 to 0.6 M, but the resolution remains low and does not enable a correct attribution of the equivalent volumes of the TBAOH.

To sum up, when titration of a pickling bath containing the mixture of HF/ HNO_3 and H_2TiF_6 was carried out by TBAOH, the curve exhibits three neutralization waves, the first one concerns both HNO_3 ($\times 1\text{H}^+$) and H_2TiF_6 ($\times 1\text{H}^+$), while the second and third were not rigorously identified. Besides, because the TBAOH is a relatively unstable basis and it decomposes in contact with the air/moisture, only potash will be used in the next sections.

2) Influence of the aluminum concentration ($\text{Al}(\text{NO}_3)_3, 9\text{H}_2\text{O}$) on the acid-base titrations of a mixture of acids HNO_3/HF

The aluminum is another metal contained into the titanium alloys (**Table 1**). $\text{Al}^{(\text{III})}$ is also known to be complexed by fluoride ions [15] and this section expects to examine the plausible reaction of the complex $\text{Al}^{(\text{III})}/\text{fluoride}$ (produced by the pickling of titanium alloys) with KOH (0.85 M in the ethanol solvent) and to determine possible interferences on the waves of the neutralization of HNO_3 and HF. Nona-hydrated salt of aluminum nitrate was added, into the pickling bath HNO_3/HF , at various mass concentration in agreement with the aluminum contents into the pickling baths (**Figure 3(a)**) 0.03 M/0.75g/L to 0.085 M/2.28g/L.

The $\text{pH} = f(V_{\text{KOH}})$ curves (a) show that the volume required for the first neutralization (V_{e1}) increases with the addition of aluminum nitrate, while the volume used for the 2nd neutralization decreases and the overall volume of KOH to neutralize the mixture remains constant! The total acidity neutralized for each wave was plotted versus the aluminum nitrate added quantity (**Figure 3(a1)** and **Figure 3(b1)**).

A linear evolution was observed for both the first and the second neutralization, and the obtained correlations were indicated in the caption of the **Figure 3**.

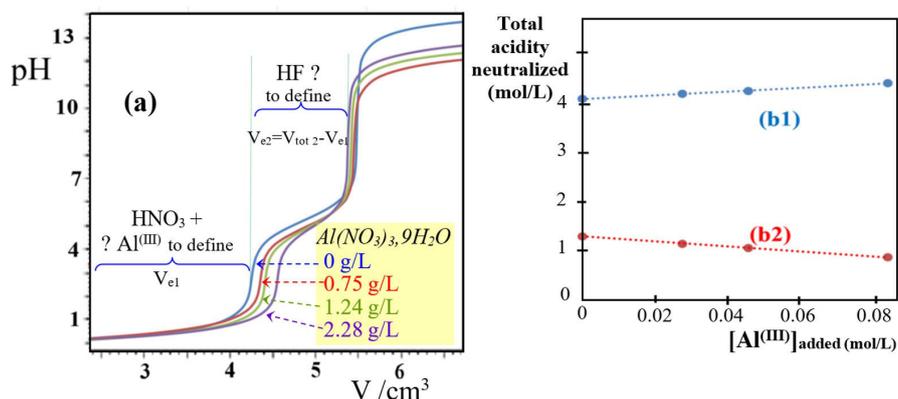
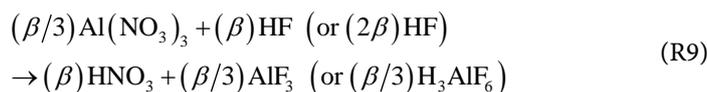


Figure 3. Titration curves of the mixture HNO_3 4 M, HF 1.3 M and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, by KOH (0.85 M) in ethanol. Room temperature, agitation, Metrohm Toledo 888 titrator, solvotrode. Quantity of the solution to be titrated: 1 mL, diluted using ethanol into a final volume of 50 mL. (a) $\text{pH} = f(V_{\text{KOH}})$ curves obtained at three different concentrations of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. (b1) Total acidity determined from the Ist wave (V_{e1}):

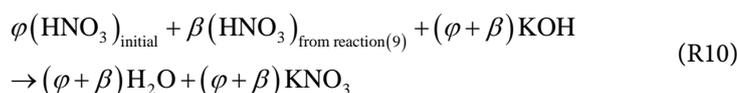
$[\text{HNO}_3] + \lambda \times [\text{Al}^{(\text{III})}] = 4.02 + 3.7 \times [\text{Al}^{(\text{III})}] R^2 = 0.99$ (e3). (b2) Total acidity determined from the II^d wave (V_{e2}): $[\text{HF}] + \mu \times [\text{Al}^{(\text{III})}] = 1.26 - 3.7 \times [\text{Al}^{(\text{III})}] R^2 = 0.99$ (e4).

The slope value of 3.7 was obtained for the first neutralization, while the value of -3.7 was found for the second neutralization.

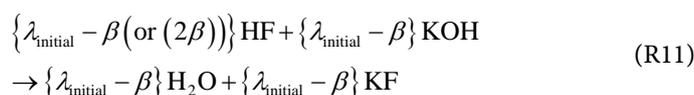
The following reactions could be proposed:



Ist neutralization:



II^d neutralization:



One aluminum complexes 3 fluorides and provides 3 nitric acids that explains the decreases of the second neutralization volume (HF) and the increases of the first one (HNO_3).

Note that if H_3AlF_6 is formed (R9), there is no change in the volume of KOH required for both neutralizations. Indeed, in this scenario, the 3 additional HF consumed were compensated by the 3 protons released by H_3AlF_6 which appears here as a weak acid, similar to HF.

Concerning the other metallic cations susceptible to be released by the titanium alloys (**Table 1**) into the pickling bath, their effect on the volume of the titrating basis required for the neutralization, was not investigated in the present study. Indeed, their overall mass content does not exceed 5%, and the most important are: V (~5%, $d = 5.9$), Mo (~5%, $d = 10.2$) and Cr (~3%, $d = 7$); taking

into account their high density, compared to this of titanium ($d = 4.5$), we can conclude that their molar composition is relatively low (<4%) and can be neglected for the determination of HF and HNO_3 concentrations of the titanium pickling baths.

To conclude, when the pickling bath contains cations such as $\text{Ti}^{(\text{IV})}$ or/and $\text{Al}^{(\text{III})}$ it arises their complexation by fluoride ions, reactions releasing protons which behave as strong acid and neutralize during the first wave (simultaneously to HNO_3). Consequently we can conclude that the first neutralization wave in the curve $\text{pH} = f(V_{\text{titrating basis}})$ concerns, at the least three species: nitric acid, titanium and aluminum adducts.

The second neutralization volume, (corresponding to the HF in the case of an initial pickling bath) is also affected by the presence of the cations released by the alloys pickling, especially aluminum.

So it appears difficult to determine, by the use of single potentiometric titrations alone, the concentration of both acids (HNO_3 and HF) into a solution which has been “largely” used to pickle titanium alloys. ICP was employed to determine the concentrations of Al(III) and Ti (IV), and we propose following way for the monitoring of the concentration of HNO_3 and HF into the pickling bath:

To access to the nitric acid concentration, the Equation (e5) must be used:

$$\begin{aligned} & \text{moles of } \text{HNO}_3 \text{ into the pickling bath titrated volume} \\ & = \text{moles of KOH used in the first neutralization } (V_{e1}) \\ & \quad - 2 \times \text{moles of } \text{Ti}^{(\text{IV})} \text{ determined by ICP} \\ & \quad - 3 \times \text{moles of } \text{Al}^{(\text{III})} \text{ determined by ICP} \end{aligned} \quad (\text{e5})$$

To access to the hydrofluoric acid concentration, the Equation (e6) must be used:

$$\begin{aligned} & \text{moles of HF into the pickling bath titrated volume} \\ & = \text{moles of KOH used in the II}^d \text{ neutralization } (V_{e2} = V_{\text{tot2}} - V_{e1}) \end{aligned} \quad (\text{e6})$$

3.2.2. Alloys of the Stainless Steel

In this section we examine mixtures exclusively devoted to pickle alloys of the stainless steel. The most abundant elements of these alloys are the iron, the chromium and the nickel (Table 1). The effect of the concentration of these metallic cations on the waves of the neutralization of HNO_3 and HF (curves $\text{pH} = f(V_{\text{titrating basis:KOH}})$) was examined with the same objective as previously: to try to define a reliable method enabling the monitoring of the acidic contents of the industrial pickling baths initially containing these acids.

1) Influence of the iron $\text{Fe}^{(\text{III})}$ concentration on the titration by KOH of the mixture “ HNO_3/HF ”

The iron is the main metal ($60 \leq \text{mass percent} \leq 80$) constituting the stainless steel alloys. The cations released after the pickle of the alloy, especially $\text{Fe}^{(\text{III})}$, are able to complex with the fluoride anions to form compounds such as FeF_3 or H_3FeF_6 [16]. The influence of the $\text{Fe}^{(\text{III})}$ on the volume of the titrating base (KOH

1 M in ethanol) required to neutralize HNO_3 and HF was examined. To that end titrations of baths containing both acids were performed by adding iron(III) nitrate at various concentrations.

In the examined concentration range, the obtained curves $\text{pH} = f(V_{\text{KOH}})$ **Figure 4(a)**, exhibits two neutralization waves; increasing the concentration of the nitrate-iron-added cause the volume of the first neutralization (previous attributed to the HNO_3) to increase, while, simultaneously the volume required for the second neutralization decreases. Moreover the total volume of KOH used for the neutralization remains constant in the examined range. Curves presented on the right (**Figure 4(b1)**, **Figure 4(b2)** and **Figure 4(c)**) give the effect of the added iron concentration ($\text{Fe}(\text{NO}_3)_3$) on the evolutions of the acidity determined from: the first (b1) or the second (b2) neutralization waves, as well as from the sum of the first neutralization wave and the “known” added iron content (c). A linear evolution was observed for all cases, the obtained slopes inform on the number of the involved “equivalent H^+ ”, in the corresponding neutralization. Thus, concerning the first neutralization wave (b1), the slope found is equal to 5.7, (considered equal to 6), means that the addition of 1 mole of $\text{Fe}(\text{NO}_3)_3$ leads to the creation of a number of equivalent H^+ which reacts and neutralizes 6 moles of the KOH.

Simultaneously, curve (b2), concerning the second neutralization wave (*and*

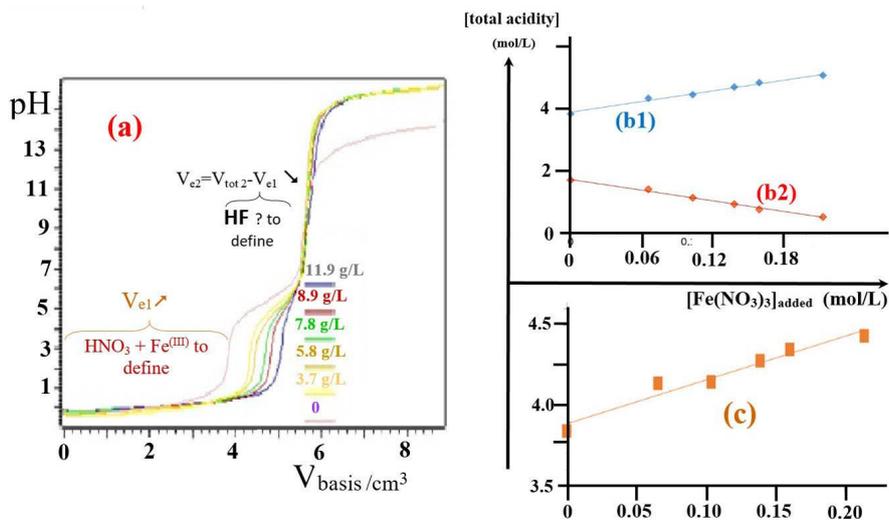


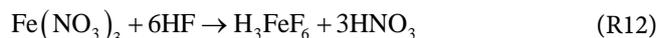
Figure 4. Acid-Base titration curves of the mixture containing HNO_3 (3.8 mol/L), HF (1.7 mol/L) and (nonhydrated $\text{Fe}(\text{NO}_3)_3$) at various concentrations (a). KOH (1M) is the titrating basis present in ethanol. Room temperature, agitation, Metrohm Toledo 888 titrator, solvotrode. Quantity of the solution to be titrated: 1 mL, diluted into a final volume of 50 mL (completed using ethanol). Right: effect of added $\text{Fe}(\text{NO}_3)_3$ concentration on the total acidity determined from: (b1) the Ist neutralization:

$$[\text{HNO}_3] + \eta * [\text{Fe}(\text{NO}_3)_3] = 3.9 + 5.7 * [\text{Fe}(\text{NO}_3)_3] \quad R^2 = 0.99 \quad (\text{e7}).$$

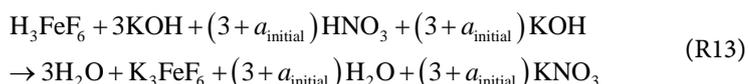
$$[\text{HF}] + \lambda * [\text{Fe}(\text{NO}_3)_3] = 1.7 - 5.7 * [\text{Fe}(\text{NO}_3)_3] \quad R^2 = 0.99 \quad (\text{e8}).$$

$$[\text{acid } j] = 3.9 + 2.7 * [\text{Fe}(\text{NO}_3)_3] \quad R^2 = 0.96 \quad (\text{e9}).$$

giving the evolution of the concentration of the remaining HF, after reaction with the iron nitrate) exhibits a negative slope, find equal to -5.7 , clearly shows that one molecule of iron consumes six molecules of HF. The following reaction scheme can be proposed to explain these evolutions: the iron added complexes with the fluoride of the hydrofluoric acid HF:



Both the obtained tri-acid H_3FeF_6 and the nitric acid as well as the nitric acid initially present in the bath, react simultaneously during the first neutralization wave (V_{e1}) by the basis according to:



Then, the neutralization of the “remaining free HF” occurs. The curve shown in the **Figure 4(c)**, presents the evolution of the concentration of the nitric acid (obtained by subtracting at the first neutralization volume (V_{eq1}), three fold the quantity of the iron nitrate), as a function of $\text{Fe}(\text{NO}_3)_3$ added. The obtained slope equal to 2.7 and considered to be equal to 3 , clearly shows that one molecule of iron added in the mixture creates an equivalent number of three supplementary protons to be neutralized.

In conclusion of this section, when iron cation is added in the HNO_3/HF bath, the overall neutralization volume of KOH (V_{tot2}) is not affected; however both the volumes of the first and the second neutralization (respectively V_{e1} and V_{e2}) were affected. Moreover direct precipitation of $\text{Fe}(\text{OH})_3$ was not observed.

From these results it can be proposed the following equations:

$$\begin{aligned} &\text{moles of KOH used in the first neutralization}(V_{e1}) \\ &= \text{moles of HNO}_3 \text{ into the pickling bath titrated volume} \\ &+ 6 \times \text{moles of Fe}^{(\text{III})} \text{ introduced} \end{aligned} \quad (\text{e10})$$

$$\begin{aligned} &\text{moles of KOH used in the II}^{\text{d}} \text{ neutralization } (V_{e2} = V_{\text{tot2}} - V_{e1}) \\ &= \text{moles of the free HF into the pickling bath titrated volume} \end{aligned} \quad (\text{e11})$$

2) Influence of the chromium ($\text{Cr}(\text{NO}_3)_3, 9\text{H}_2\text{O}$) on the acid-base Titrations of a HNO_3 , HF pickling bath

The chromium is introduced in relatively important quantities into the stainless steel alloys ($14 < \text{Cr}_{(\text{mass} \%)} < 20$). The cations released after the pickle of the alloy, especially $\text{Cr}^{(\text{III})}$, are able to complex with the fluoride anions to form compounds such as CrF_3 , CrF_2^+ or CrF^{2+} [17], however the complexation constants appear to be relatively low ($< 10^4$); besides no information were found about complexation of $\text{Cr}^{(\text{VI})}$ and F^- . The influence of the $\text{Cr}^{(\text{III})}$ on the volume of the titrating base (KOH) required to neutralize HNO_3 and HF was examined as previously (adding chromium nitrate at various concentrations, chosen in function of the weight % of Cr into the stainless steels), and the results were presented in **Figure 5(a)**.

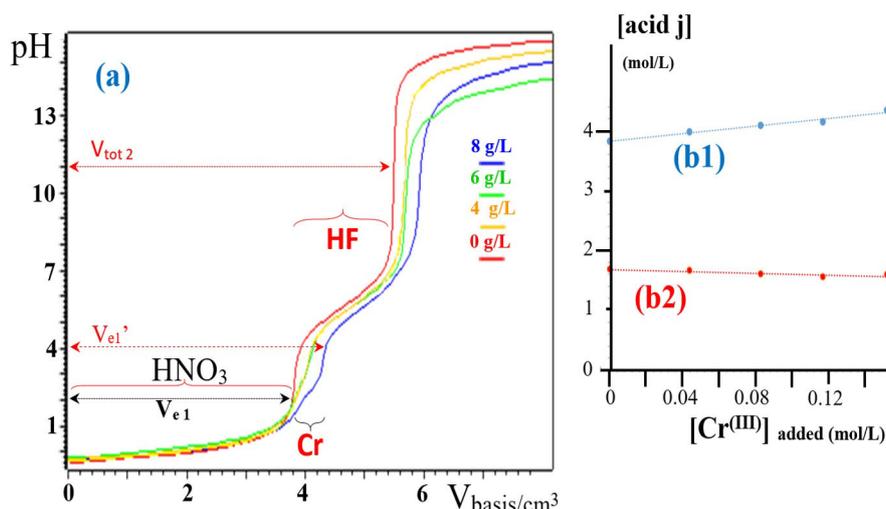


Figure 5. Acid-Base titration curves of the mixture containing HNO_3 (3.8 mol/L), HF (1.7 mol/L) and $\text{Cr}(\text{NO}_3)_3$ at various concentrations (a). KOH (1 M) is the titrating basis present in ethanol. Room temperature, agitation, Metrohm Toledo 888 titrator, solvotrode. Quantity of the solution to be titrated: 1 mL, diluted in ethanol into a final volume of 50 mL. **Right:** Effect of added $\text{Cr}(\text{NO}_3)_3$ concentration on the total acidity determined:

-(b1) from the neutralization volume $V'_{\text{eq}1}$:

$$[\text{HNO}_3] + \mu * [\text{Cr}^{(\text{III})}] = 3.8 + 3.2 * [\text{Cr}^{(\text{III})}] R^2 = 0.97 \quad (\text{e}12)$$

-(b2) from the neutralization volume $V_{\text{eq}2} - V'_{\text{eq}1}$:

$$[\text{HF}] + \eta * [\text{Cr}^{(\text{III})}] = 1.7 - 0.7 * [\text{Cr}^{(\text{III})}] R^2 = 0.77 \quad (\text{e}13).$$

Analysis of the titration curves leads to the following remarks:

- the KOH volume required for the first neutralization (V_{e1}) remains practically constant versus the added Cr concentration, meaning that the presence of chromium does not affect the nitric acid neutralization wave.

- a new neutralization wave appears in second position (pH~2), and the corresponding “neutralization volume” ($V'_{\text{eq}1} - V_{e1}$) increase with the concentration of the added chromium; this wave is consequently attributed to the reaction of the added chromium with the potash.

- the third wave (previously attributed to the HF) shifts to the right (to the higher volumes of KOH), however its volume ($V_{\text{tot}2} - V'_{e1}$) remains constant. These observations mean that, in the operating conditions, the presence of the chromium does not affect the neutralization volume of the HF; this implies a “no-strong complexation” between both species and is in agreement with the values of the equilibrium constants proposed in [17].

As the waves of HNO_3 and Cr are very close, it is preferable to measure the overall volume of potash ($V'_{\text{eq}1}$) used. Thus, the graph (b1) in Figure 5 present the total acidity neutralized during the first and the second wave (determined by the potash volume V'_{e1} , *i.e.* nitric acid+chromium) versus the concentration of the added chromium. The slope of this curve (~3) correspond to the moles of potash used to neutralize the chromium added, consequently we propose the corresponding reaction: ($\text{Cr}^{3+} + 3\text{OH}^- \rightarrow \text{Cr}(\text{OH})_3$).

The graph (b2) in the same **Figure 5** presents the acidity neutralized during the third wave (determined by the potash volume $V_{\text{tot}2} - V'_{e1}$, *i.e.* hydrofluoric acid) versus the concentration of the added chromium. The obtained curve is practically a horizontal line (slope ~ -0.7) meaning that even if a complexation of the Cr^{3+} occurs by the fluoride, it is not strong enough to introduce significant error in the determination of the concentration of the HF.

From these results it can be proposed following equations:

$$\begin{aligned} & \text{moles of KOH used in both the I}^{\text{st}} \text{ and II}^{\text{d}} \text{ neutralization } (V'_{e1}) \\ & = \text{moles of HNO}_3 \text{ into the pickling bath titrated volume} \quad (\text{e14}) \\ & + 3 \times \text{moles of Cr}^{(\text{III})} \text{ introduced} \end{aligned}$$

$$\begin{aligned} & \text{moles of KOH used in the III}^{\text{d}} \text{ neutralization } (V_{e2} = V_{\text{tot}2} - V'_{e1}) \quad (\text{e15}) \\ & = \text{moles of the free HF into the pickling bath titrated volume.} \end{aligned}$$

Note that in the industrial pickling bath, the maximum concentration of the chromium cannot exceeds 0.08 mol/L, *i.e.* 4 g/L (if yes the bath is renewed); if this maximum concentration is neglected (*i.e.* if V'_{e1} is totally attributed to the neutralization of the nitric acid) then the introduced error (0.24 mol/L) reaches 6% of the initial concentration of the HNO_3 .

3) Influence of the nickel ($\text{Ni}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) on the acid-base Titrations of a HNO_3 , HF pickling bath

The nickel is another metal present in significant quantities ($4 < \text{Ni}_{(\text{mass} \%)} < 20$) into the stainless steel alloys. As previously the influence of the nickel nitrate concentration on the volume of the titrating base (KOH) required to neutralize HNO_3 and HF was examined in order to determine if $\text{Ni}^{(\text{II})}$ cations released after the pickle of the alloy, are strongly complexed by the fluoride anions to form compounds such as NiF_2 , and the results were presented in **Figure 6(a)**.

Analysis of the titration curves (a) leads to the following remarks:

- the KOH volume required for the first neutralization (HNO_3) remains constant versus the added $[\text{Ni}^{(\text{II})}]$. Indeed, curve b1 in the **Figure 6**, corresponding to the added $[\text{Ni}^{(\text{II})}]$ dependence on the moles of KOH used for the first neutralization wave (V_{e1}), appears as a straight line having a slope relatively low (~ -0.3), which could be considered as equal to zero;
- in a similar manner, the KOH volume required for the neutralizations occurring in the second part of the curve (II^{d} and III^{d} waves, *i.e.* V_{e2}) remains practically constant versus the added $[\text{Ni}^{(\text{II})}]$ concentration. Indeed, curve b2 in the **Figure 6**, corresponds to the added $[\text{Ni}^{(\text{II})}]$ dependence on the moles of KOH used for the neutralizations of the II^{d} and III^{d} waves, also appears as a straight line having a slope of +0.2, a value which could, in the operating conditions, be considered as equal to zero;
- the overall KOH volume (V_{e1} and V_{e2}) required for all neutralizations remains constant versus the quantity of the Nickel added;
- the third wave corresponds to the free HF neutralization;
- a new neutralization wave (a shoulder in fact), appears in second position (pH ~ 4) when $\text{Ni}^{(\text{II})}$ was added. The presence of a wave, coupled to the fact that

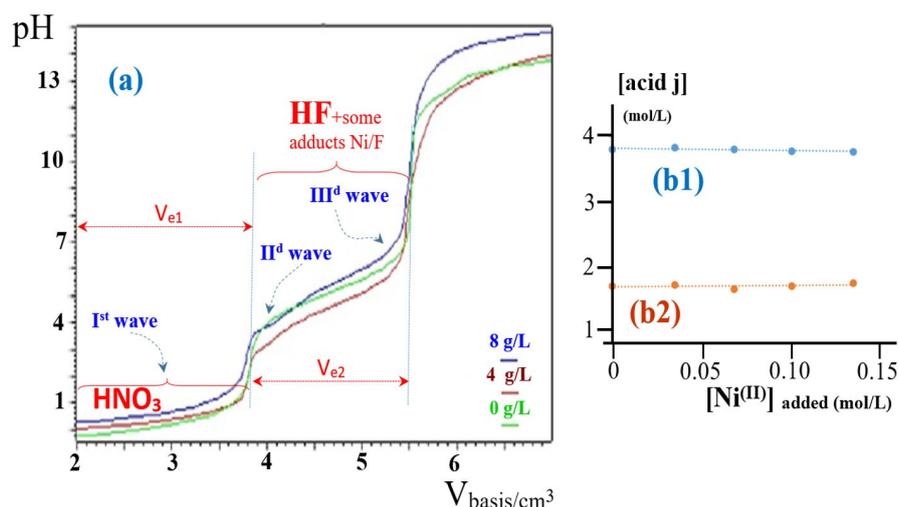


Figure 6. Acid-Base titration curves of the mixture containing HNO_3 (3.8 mol/L), HF (1.7 mol/L) and $\text{Ni}(\text{NO}_3)_2$ at various concentration (a). KOH (1 M) is the titrating basis present in ethanol. Room temperature, agitation, Metrohm Toledo 888 titrator, solvotrode. Quantity of the solution to be titrated: 1 mL, diluted using ethanol into a final volume of 50 mL. Right: Effect of added $\text{Ni}(\text{NO}_3)_2$ concentration on the total acidity determined: -(b1) from the neutralization volume V_{e1} : $[\text{acidity}] = 3.8 - 0.3 * [\text{Ni}^{(\text{II})}] R^2 = 0.7$ (e16). -(b2) from the neutralization volume V_{e2} : $[\text{acidity}] = 1.7 + 0.2 * [\text{Ni}^{(\text{II})}] R^2 = 0.2$ (e17).

the neutralization volume (V_{e2}) remains practically constant, implies a possible complexation between HF and nickel (II). Two possibilities could be involved to explain this behavior: 1) a complexation occurs between HF and nickel (II), consuming x HF and leading to a complex exhibiting $x \text{H}^{(+1)}$ to neutralize, without modification of the required volume of KOH, and 2) $\text{Ni}^{(\text{II})}$ and HF react according to a more complicated equilibria. However, the equilibrium constants of all these reactions are low and during the titration of the HF, the equilibria shifts-back to regenerate the HF.

Moreover,

- the low resolution of this intermediate wave also confirms the low value of this equilibria. The following simple reactions could be proposed:



In these conditions a simple titration does not enables to determine a precise value for the coefficient x (of $\text{H}_x\text{NiF}_x^{2+}$), even if it is obvious that the presence of $\text{Ni}^{(\text{II})}$ does not affects the volume required to titrate the HF (*i.e.* $x \sim 0$). In fact, the pickling bath were replaced when the concentration of Ni reaches a maximum of 0.068 mol/L (4 g/L), and here the second wave appears only when the Ni concentration reaches 0.14 mol/L (8 g/L) **Figure 6(a)**.

Note that the precipitation of $\text{Ni}(\text{OH})_2$ was not observed in the operating conditions, because its high pK (around 6 in aqueous media, probably higher in

ethanolic media).

Consequently, for the monitoring of the acidic content in the pickling bath, we can neglect the potash volume devoted to an eventual neutralization of the nickel cations, and following equations could be proposed:

$$\begin{aligned} & \text{moles of KOH used in the I}^{\text{st}} \text{ neutralization } (V_{e1}) \\ & = \text{moles of HNO}_3 \text{ into the pickling bath titrated volume} \end{aligned} \quad (\text{e18})$$

$$\begin{aligned} & \text{moles of KOH used in both the II}^{\text{d}} \text{ and the III}^{\text{d}} \text{ neutralizations } (V_{e2} = V_{\text{tot2}} - V_{e1}) \\ & = \text{moles of the free HF into the pickling bath titrated volume} \end{aligned} \quad (\text{e19})$$

Note that the other metallic cations released by the pickle of the stainless steels could be neglected, their mass percent remains low ($\leq 4\%$).

To sum up concerns the stainless steel alloys, taking into account the results of the titrations of the cations released by the pickle of the alloys, we propose the following way to monitor the concentrations of HNO_3 and HF into the pickling bath:

To access to the nitric acid concentration, the following equation must be used:

$$\begin{aligned} & \text{moles of HNO}_3 \text{ into the pickling bath titrated volume} \\ & = \text{moles of KOH used in the first neutralization } (V'_{e1}) \\ & \quad - 6 \times \text{moles of Fe}^{(\text{III})} \text{ determined by ICP} \\ & \quad - 3 \times \text{moles of Cr}^{(\text{III})} \text{ determined by ICP} \end{aligned} \quad (\text{e20})$$

To access to the hydrofluoric acid concentration, the following equation must be used:

$$\begin{aligned} & \text{moles of HF into the pickling bath titrated volume} \\ & = \text{moles of KOH used in the II}^{\text{d}} \text{ neutralization } (V_{e2} = V_{\text{tot2}} - V'_{e1}) \end{aligned} \quad (\text{e21})$$

3.3. Titration of Real Pickling Baths

Several experiments were achieved to try to validate the above obtained results; typically, pickling of all the alloys indicated in the **Table 1** were carried out using baths initially containing nitric acid and HF; titrations of each pickling bath were performed each 20 min during 2 h and simultaneously the above involved metallic cations were titrated by ICP. Results were compared to the mass loss of the alloy at the end of each pickle. As an example, typical values obtained with the alloy TA **Table 1** agree with the stoichiometry of the reaction (R6) and confirm the validity/reliability of the method.

For another alloys, results (and specifically the evolution of the concentration of HF) appears coherent with the pickling rate of the alloy (the rate reaches zero for HF concentrations close to 0.3 M).

Note that for alloys containing zirconium, after pickling, it is observed into the bath precipitates attributed to the zirconium which does not oxidize at the operating conditions

Besides, it is impossible (in our knowledge) to absolutely validate the obtained

results, e.g. the concentration of each acid, especially in presence of metallic cations; indeed most of the analytical available methods needs dilution, and this operation is able to modify the equilibria between the various species so to lead to erroneous results.

The proposed method is satisfactory because it takes account of the interfering metallic cations, as well as their contribution (stoichiometric factors on the neutralization reactions) on the potash volume required for the neutralization of both acids. The main drawback is that the determination of the metallic cations requires ICP, a relatively sophisticated and also expensive analytical method, even if it is required to analyze the metallic ions content before to regenerate, by various processes, the pickling bath for a new cycle [18] [19].

4. Conclusions

The content of the acids contained in the pickling bath used in the aeronautical industries must be monitored in order to ensure uniform pickle for all the treated pieces. Even if various methods were proposed in the bibliography, the results were not reliable and sometimes strong dispersion can be observed between the results of sub-contracting operators. In the present study, acid-basis titration by potash, monitored by pH metry, was chosen and a systematic analysis of the effect of the metallic cations “in majority into the alloys” was carried out, into the ethanol in order to limit the precipitation of the metallic hydroxides. The $\text{pH} = f(V_{\text{KOH}})$ curve obtained with an initial composition bath, exhibits two waves respectively attributed to the neutralization of nitric and hydrofluoric acids. In general, the pickling of the alloys produces cations which were complexed by fluoride ions and the resulting adducts behave as acids, able to be neutralized by KOH in a similar way as HNO_3 and HF.

For the titanium alloys, results clearly demonstrates interferences (on the neutralization curve) with the $\text{Ti}^{(\text{IV})}$ and $\text{Al}^{(\text{III})}$ while for stainless steels alloys interferences were observed with iron and chromium: all these cations complexes with fluoride, thus consuming HF. A possibility to simplify the titration is to use separated bath to pickle the titanium and the stainless steel alloys.

To deduce the concentration of the hydrofluoric acid, the KOH volume used to neutralize the second wave of the curve $\text{pH} = f(V_{\text{KOH}})$, can be directly used *i.e.* Equation (e6) for the titanium alloys and (e21) for the stainless steel alloys. Note that the V_{KOH} can be disturbed by the neutralization of the nickel cations: here we neglect this species because: 1) the shoulder indicating the presence of nickel appears on the curve for contents of nickel higher than the maximum that is possible to reach for the highest time life of the bath; and 2) the nickel fluoride complex appears to have a low stability constant.

The determination of the concentration of the nitric acid is more complicated, as two metallic ions (per family of alloys) interfering on the neutralization of the first wave; indeed at the least three metallic cations ($\text{Ti}^{(\text{IV})}$, $\text{Al}^{(\text{III})}$ and $\text{Fe}^{(\text{III})}$) complexes with fluoride and produces strong acids which neutralize simultaneously

with nitric acid! In addition, neutralization of $\text{Cr}^{(\text{III})}$ by OH^- was also observed near the first neutralization. To overcome this drawback, it is proposed to use ICP to determine the concentrations of the cations such as iron and chromium for stainless steel alloys and titanium and aluminum for titanium alloys. Then titration of the pickling bath by KOH provide the curve $\text{pH} = f(V_{\text{KOH}})$, of which the potash volume used to neutralize the first wave enables to access to HNO_3 content, thanks to the established Equations (e5) for the titanium alloys and (e20) for the stainless steel alloys.

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