Adsorption and Desorption of Metals

by

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INTRODUCTION

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) was used with different acidic solutions to study metal adsorption and desorption to indicate possible problem sources in ultrapure chemical systems in some semiconductor processes. This complex evaluation of the metal adsorption and desorption shows that the cleanliness of ultrapure processes cannot be characterized by the cleanliness of the chemicals only. For adequate evaluation, the entire system needs to be considered, taking into account the specific behavior of each component, e.g., adsorption and ion-exchange properties of system walls, complex formation constants of different metals in the solution, kinetic and equilibrium data of reactions inside the solution, and with the active sites of the system wall, and the rate of the mass transport processes.

The importance of trace metal adsorption and desorption is well known in the semiconductor industry (1-5,10). This study intends to examine a deeper understanding of the chemical mechanism of metal transport processes on and near surfaces which are in contact with ultrapure chemicals. The results of this paper demonstrates the role of metal complex formations in real wet chemical systems by showing the typical acid dissolution effects with different metals and materials.

ICP-MS sample introduction systems (SIS) were used to illustrate the adsorption/desorption phenomena. Similar metal adsorption phenomena was seen on the ion signals using direct injection nebulization with ELAN 250 ICP-MS and also on the Teflon coated inert spray chamber with VG PlasmaTrace high resolution ICP-MS by Koch and Settembre (20,21), during measurement of heavy metals, and especially in case of lantanides during a standard stability study. Neither the transient signal behavior resulting from specific metal adsorption processes on the system wall nor the importance of these processes in the measuring system in case of very low concentration level measurements was shown in their study.

RESULTS

An ICP-MS system was selected for studying metal surface phenomena because metal concentration changes can be directly measured within seconds after the reactions; therefore, identification and interpretation of the processes are easier. Figure 1. shows that different ions behave in different ways. When standard is aspirated, the increase of ion signal of lead is far slower than it is for lithium, copper and cadmium, and it reaches the plateau some minutes later. After rinsing with DI water, when 3% nitric acid is aspirated, a large lead ion peak is observed with up to 2-8 times higher concentration than the steady state signal of lead. During 3% nitric acid rinse, copper gives a smaller peak, cadmium gives an even smaller one, while no lithium peak is observed. All these peaks return to the baseline within 3-5 minutes during the 3% nitric acid aspiration, showing that the 3% nitric acid was not contaminated. The total amount of adsorbed metals can be calculated from the integrated intensity. There are large differences in the total amount of adsorbed material for different metals, i.e., 'selective adsorption' of some heavy metals is found. This type of large selectivity generally cannot be explained by physical adsorption/desorption processes, but can be explained by ion-exchange or by complex formation processes.

A set of similar experiments was conducted using three different ELAN 250/500 ICP-MS, sample introduction systems (SISs) with three types of nebulizer and spray chambers:

1. **Ultrasonic nebulizer (USN)** - alumina transducer head and glass spray chamber, heating and cooling loop. This has the largest surface area, most of which is glass.
2. **Cross-flow nebulizer** with Ryton spray chamber - Most surfaces are plastic with poly(phenylene-sulfide) polymer.
3. **Meinhardt C3 concentric nebulizer** - Glass spray chamber. Most surfaces are glass. Inlet tubes are Tygon and Teflon.

Another set of experiments was performed using polyethylene and FEP DI water bottles. After standard was stored in the bottle, the inner wall of the bottles was scanned using different acid solutions. The role of the complex formation in the solution was also demonstrated by a wafer cleaning experiment using 6 inch wafers, SC1 and SC2 solutions, and citric and tartaric acids as complex forming ligands in the solution. The difference of bulk material contamination and metal adsorption on surface is discussed in connection with acid digestion blanks of PFA and Teflon tubes.

In order to show both the differences between different acids and, to some extent, the effect of acid concentration, 1, 2 and 3% nitric acid, 1 and 2% HCl, 0.5, 1 and 2 % HF was used for rinsing. However, the major emphasis was on the chemical behavior of different metals with different acids and not on chemical kinetics of the reactions with different acid concentrations. Each time, the ion signal of 5-8 metals was monitored during the acid rinse and the ion signal was compared to the background signal of the DI water rinsing cycle and sometimes with the signal of a standard with known concentration. Metal ion standards were also used both for the measurement and for contamination studies.

Since most trace metal adsorption/desorption phenomenon showed up similarly in each SIS, the resulting data from these experiments are shown together without emphasizing the differences between different SIS's. One remarkable difference, however, was the different adsorption capacity on USN which showed a higher metal adsorption, i.e., memory effect, than the other two systems. The lowest metal adsorption was found on the Meinhardt C3 nebulizer with glass spray chamber. Due to the fact that the USN has the best sensitivity and the largest surface area, the trace metal adsorption is therefore amplified. Consequently, these USN data were primarily selected for presentation.

The desorption experiments were run after routine sample measurements and after the measurement of all trace metal standards. Therefore, the walls of the sample introduction systems were already loaded with several metal ions.

The best example of specific trace metal adsorption/desorption is shown on Figure 2, with the desorption characteristics of bismuth (Bi), palladium (Pd), lead (Pb) and tantalum (Ta) in the USN. In DI water, all four ions have a baseline of approximately 10 cps. Aspirating 1 % nitric acid causes a tenfold increase of the ion signal; however, the Bi ion signal does not show a significant change. In 1 % HCl, the Ta and Pd ion signal increases about 10 times, and the lead ion signal about 50 times. The Pd signal decreases back to the baseline level relatively fast, but the Ta and Pb ion signal remains stable. The increase of the Bi ion signal is approximately 3 orders of magnitude. The rinse down of Bi with 1 % HCl is relatively slow, which shows a significant Bi load on the surfaces. Aspirating 0.5 % HF for one minute releases Ta from the surface of the SIS giving a Ta peak intensity of about 80,000 cps, four times higher than the intensity of the 4 ppb standard solution! A small increase of the Bi signal was also observed. After changing to DI water solution, Ta rinses down slowly for several minutes more.

In consideration that the glass system is etched by HF solution over an extended period of time, HF solution was not aspirated for more than one minute in the USN. Tin (Sn) showed a very similar rinse characteristics to Bi with all the acids used, shown on Figure 3. Significant rinsing of Sn is not caused by 2 % nitric acid and 2% HF in the USN. However, 1 % HCl starts to slowly rinse out tin, starting with a Sn peak equivalent of approximately 40 ppb Sn.

This phenomenon can cause a very severe interference reaction in flow injection ICP-MS applications if the solution contains chloride ions, as is shown on Figs. 4 and 4.1. After standard injections, 1 % HCl blank was injected several times. Due to the adsorbed Sn on the wall, which dissolves with HCl slowly, very high Sn peaks were found, showing virtually a high Sn concentration in the HCl solution. However, these Sn peaks were decreasing during repeated injections due to the fact that smaller and smaller amounts of Sn were on the wall.

Fig. 5. shows the signal change of V, In and Pb. Fig. 6. shows Al, Mn, Sn and Co. Fig. 7. shows Pd and La. Fig. 8. shows Nb, Ta and Bi signal changes in cross-flow nebulizer with Ryton spray chamber, rinsing with HNO_3, HCl and with HF. On Fig. 9, the Cr, Ag, Cd, and Pb signal change is shown with the same acids in the Meinhardt C3 nebulizer and glass spray chamber SIS. Lead and palladium seems to be rinsed by 2% nitric acid faster in these spray chambers. However, V prefers 2% HF (Fig. 5), just like its Group Five mates, Nb and Ta (Fig. 8.). In (Fig. 5.), Cr (Fig. 9.), Co, Mn (Fig. 6.), and Ni (not shown) rinse fast from all SIS, giving a sharp peak. However, the desorption of Al and Sn is far slower (Fig. 6.).

The potential danger of these processes on trace metal measurements for a not-well-known sample matrix is shown in Table 1, as a high Ta and Nb concentration in one duplicate of two different samples. This probably results from fluoride ions remaining in the sample after the sample preparation process which can elute Nb and Ta.

Effect of Reaction Rate on Desorption Trends

The difference in the relative reaction rate of different metals on the rinse curve of Sb and Bi with 1 % HCl is shown on Figure 10. Sb rinses down significantly faster, than Bi, due possibly to the faster complex decomposition reaction. Another interesting observation is that in the flow injection sample introduction mode, Bi gives a double peak. The first one is fast and comes through with the Sb peak, but the larger second one reaches a peak when the Sb ion intensity is already decreasing and is close to the baseline (Fig. 11.). This indicates that there are at least two reactions with very different rate constants involved in the decomposition of the Bi complexes at the surface, and that the second reaction is considerably slower than the first, but results in more Bi atoms.

DISCUSSION of RESULTS

Interpretation

The specific desorption of Ta and Nb with HF and that of Bi with HCl shows that the desorption is probably not a result of a general acid desorption effect. For example, it cannot be explained simply with the competition of hydronium ions for the ion exchange sites or for the hydroxide ions in the metal hydroxide complex as in the case of some +2 charge ions, e.g., Pd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}. It seems a more probable explanation that the acid anions participate in specific complex formation reactions with the metal compounds. These reactions may help to break up the bonds of metal ions with the surface. If the metal deposition occurred in a hydroxide or hydroxide oligomer form, the rate of dissolution of trace metals from the surface will be determined by the rate of the decomposition of the metal-hydroxide complexes and by the rate of the formation of the new metal-anion complexes. The difference in reaction rates explains the different rinsing (dissolution) rate of Sb and Bi from the same surface. The dissolution of Pd shows a strong dependence on the nitric acid concentration, while other trace metals seem less effected by that. In fact, the Bi signal remains the same in 3 % nitric acid as in the DI water rinse. One explanation can be that the dissolution rate of Pd is determined by the dissolution of hydroxide with acid.

The chemical form of 'adsorption' of these metals on the surface appears to be the hydroxide complex which can form complex bonds with the Si-OH groups of the surface. According to the reaction:

$$\}\text{-Si-O-H} + (\text{H-O})\text{-M-}(\text{O-H}) + \text{H-O-Si-}\{ \;\rightarrow\; \}\text{-Si-O-M-O-Si-}\{ \; + 2\,\text{H}_2\text{O}, \qquad (17)$$

where { and } indicates the solid phase.

The +3 or +5 oxidation state of Bi, Sb, Nb, and Ta can form stable polynuclear hydroxo complexes. The decomposition of these complexes is a slow reaction, according to the general rules of complex formation and dissociation kinetics [7] about polynuclear hydroxo complexes. Niobium behaves similarly to tantalum, while antimony and thallium is similar to bismuth regarding decomposition of hydroxide complexes with HCl or HF.

The USN contains glass walls, alumina surface and plastic tubing. The most active 'adsorbers' can be the alumina surface with its very active Al-OH surface groups, and also the glass surface with active Si-OH groups which causes the metal adsorption to be the most pronounced with USN. However, the cross-flow nebulizer with a Ryton spray chamber and the concentric nebulizer with a glass spray chamber shows a similar behavior with the same metal ions, except that the adsorption capacity is smaller. The sulphur atoms in the Ryton material spray chamber may form different complexing groups on the surface, e.g. -S-H, -C=S, which forms stable complexes with heavy metals.

With an appropriate integration of the adsorption curves, if the system transition function, i.e., an ideal response curve without adsorption is known, calculation of the total amount of adsorbed metal ions on the surface of an ICP-MS system is possible. It is easier to calculate the total amount of adsorbed metals based on the desorption curves, assuming that a total desorption has occurred, or using a mathematical model for the rinse function, e.g., in case of Bi with HCl.

APPLICATION EXPERIMENTS

1. Bottle rinsing experiments

Since ion exchange, metal hydrolysis, and surface complexing can be expected on any wall, high density polyethylene and FEP sampling bottles were used for the second model system in this study. After measuring the trace metal concentration by ICP-MS and finding practically no metal at higher concentration than the detection limit in the water samples, these bottles were emptied, and the wall of the bottles was scanned with 1.5 mL dilute acid solutions, one or more of 2% nitric acid, and 1 % HCl or 1% HF solutions. The acid solution is supposed to dissolve most of the deposited trace metallic contamination from the bottle wall. That solution was measured for trace metals by flow injection ICP-MS, a technique used to measure sub mL samples. Although, the larger percentage of the bottles did not show much trace metal contamination on the wall, there were numerous bottles, both high density polyethylene and FEP type, which had significant amount of metal contamination on the wall. The most common metals found were: Al, Fe, Mg, Zn, Zr, Ni. Some of the measured values in ng unit are summarized in Table 2. Dividing that number by 500, the solution concentration in 500 mL bottle equivalent to the ng amount can be calculated. These concentration values were below the detection limit of the quadropole ICP-MS.

The **10^{10} atoms/cm^2** unit column contains calculated surface contamination data on a 6" wafer, equivalent to that amount of trace metals found on the wall of a 500 mL bottle, if that was deposited onto a wafer surface. These data give direct indications about the possibility of trace metal contamination of wafers by DI water rinsing, after the chemical cleaning of the wafers. Typically, since very similar trace metal contaminations are often found on the wafer surface, the contamination by DI water seems a possibility. These findings underline a previous conclusion (10), that ultrapure water is more complex than the pure water itself. The entire system is to be considered together since contamination from any part of the system may be transported to the end product.

Another set of polyethylene and FEP bottles was used to measure the adsorbed metals on the wall from trace metal multi-element standard solutions. The purpose of this experiment was to demonstrate whether the metals exhibiting strong adsorption in the ICP-MS system would show similar strong adsorption behavior if the acidity of the sample is very low on the plastic wall of a bottle. Also, the purpose of the study was to show that complexing in the solution may prevent adsorption on the wall, i.e., the ligands compete with each other according to their stability constants.

Two sets of standards were used: a 27 element Group I standard, containing the more common elements, e.g., Li, Na, Al, V, Cr, Fe, Ni, Zn, Sn, Cd, Pb, and a 20 element Group II standard, containing less common elements, mainly heavy metals, e.g., Nb, La, Tl, Ta, Pd, In, Bi, etc. The bottles were filled with one of these standards.

The measurement was performed using 500 mL bottles of 2 ppb standards with 0.005% nitric acid concentration stored for four days. One 0.4 ppb Group I standard with 0.001 % nitric acid concentration was also measured. After four days, these standards were measured for 68 trace metals, and a relative % decrease of trace metal contamination was calculated and compared to the initial value. After the solution measurement, the bottles were emptied and rinsed carefully three times with ultrapure DI water. Then the wall of the bottles was scanned with 1.5 mL 2% nitric acid, 1.5 mL 1% HCl and 1.5 mL 1 % HF. These scanning solutions were analyzed separately for 15-24 elements by FI-ICP-MS. Since some elements may have matrix interferences in a given acid solution, e.g., V and Cr in HCl, not every element was measured in each solution. The 2% nitric acid and 1% HCl solutions were measured using USN, and the 1 % HF solution was measured with the corrosion resistant SIS with the cross flow nebulizer. The detection limits, based on the measurement of solution blanks of the same type, were different in the different acid solutions. The highest concentration of iron was expected in the last, 1% HF solution. The detection limit was too high in this solution to get comparable data. The efficiency of DI water as a rinsing agent was shown by very low concentration of trace metals typically not adsorbing on the wall, e.g., Na, Rb, Li, Sr.

Some of the trace metals found on the wall with each scanning solution are summarized in Table 3 in ng unit. The most adsorbing heavy metals, Sn, Nb, Ta, Bi, Pd were measured at high concentration in the scanning solutions, especially in the 2. scanning 1% HCl and 3. scanning 1 % HF solutions. This also proves, that the dissolution of these metals is not simply a dissolution of hydroxides by H_3O^+ ions of the acids, but also complex formation by the anions.

Most elements were found at very low concentration. Al, Fe and Pb was detected only in small quantities, except in the 0.4 ppb 0.001% acid solution. These results demonstrate that the acidity of the solution is very important, since the lower acidity means a higher degree of hydrolysis. The weakly adsorbed trace metals or hydroxide precipitates are removed during the DI water rinse and will not be on the bottle wall. The DI rinse also removes ions due to the solution equilibria of the hydroxides and other complexes. If the percent decrease of solution concentration is compared to the amount found on the bottle wall with different scanning solutions, the conclusion for most metals is that the higher the concentration decrease in the solution, the higher the amount of the same metal on the bottle wall.

In order to prove that complex formation in the solution decreases 'adsorption' on the plastic wall, 0.2 g ammonium citrate was added into one 2 ppb Group I and one 2 ppb Group II standards, and the trace metal contamination of the bottle wall was also measured. A significantly lower amount of Sn, Nb, Ta, Pd and Bi was found on the bottle wall of this solution. This proves that the citrate ions successfully competed with the hydroxide ions and with the active sites of the bottle wall for the trace metal ions. With the addition of ammonium citrate, the acidity of the solution is decreased and not increased, i.e., there was also more hydroxide ions to hydrolyze the metals.

See data in Table 3 for comparison. This is in perfect agreement with the finding during the wafer cleaning experiment detailed below.

Typically, these findings show that the same trace metals tend to adsorb on the bottle wall, than occurred in the ICP-MS SIS's. A smaller degree of adsorption of Al, Fe, and Sn, and a very strong adsorption of Sn, Nb, Ta and Bi was found.

2. Leaching of trace metals from PFA and teflon dishes: contamination from the bulk material

There is a distinct difference between the contamination behavior of adsorbed trace metals and trace metal contamination from the bulk material. There is a good chance, that trace metals from the wall can be cleaned by using the appropriate chemistry. However, cleaning trace metals from the bulk material is virtually impossible. This is illustrated by data in Table 4. Teflon and PFA dishes were cleaned in three different hot aggressive acid combinations. After the cleaning, a digestion procedure was performed with some drops of ultrapure acids, which evaporated from the dishes at a temperature of 110-130 °C. After this procedure, the trace metals from the wall were dissolved by 1 mL 2% nitric acid solution and analyzed by FI-ICP-MS. One typical contamination found in each set of dishes was copper. Different sets ordered at different times, i.e., from different manufacturing lots, gave very different copper contamination. Since several repeated cleaning and digestion procedures show the same results, the conclusion was, that:

1. There is significant amount of copper contamination in some PFA and Teflon materials.
2. It is virtually impossible to clean these materials to that extent that no copper

contamination will be found at high temperature application.

Similar high aluminum contamination was also found in some Teflon dishes. Since cold acid rinses of the wall did not show significant amounts of copper, the source of the copper using hot acids is believed to be caused by the accelerated diffusion rate of Cu in Teflon material at higher temperature in the presence of acid vapors. This example shows that both adsorption type and bulk contaminations need to be considered when using materials which are believed to be ultraclean.

3. Wafer cleaning vs. complex formation

One experiment was performed to support the role of competitive complex formation. Wafers were 'cleaned', in fact, contaminated with SC1 solution contaminated with 650 ppb trace metals. Wafers from the same lot were also cleaned in the same SC1 solution containing 1 g/L tartaric acid and 1 g/L citric acid. After 'cleaning', the wafers were rinsed and the surface concentration of trace metals was analyzed by VPD-FI-ICP-MS technique. Trace metal surface concentrations are summarized in Table 5. These data directly prove that competitive reactions between complex forming ligands for the trace metals may play a very significant role in surface contamination.

Explanations based on complex formation equilibria are considered important when trying to understand surface interaction. There is a wide range of chemical studies about complex formation and surface concentration [10-19], using mainly the phenomena for trace metal preconcentration [25]. Here similar explanations for a similar phenomenon is used. i.e., both the adsorption and desorption processes of the metals in a system will be determined by the chemical properties of the surface, including the presence of complexing ligands on the surface and the chemical properties of the trace metals, stability of hydroxides, poliacids, and complexes with other ligands.

The strong adsorption of metals, like Sn, Sb, Bi, Cd, Ta, Nb, Al, Fe can be attributed to the stability of their hydroxides, hydroxocomplexes, and to the ability of the formation of homopolyacid and hetereopolyacid structures, i.e., O-M-O-M-O chains. These hydroxocomplexes can react with other hydroxogroups of the plastic or glass surface, e.g.:

-Si-O-Me-O-M and -C-O-M-O-M,

forming strong complexes which are generally stable even in a polar solvent like water.

The desorption of metals from the surface means the decomposition of their very stable homo- and heteropolyacid structures and also the stable hydroxocomplexes. HF and HCl are both efficient acids for this 'elution' process because they form fluoride and chloride complexes with a lot of metals. However, different metals prefer different ligands. For example, Ta forms very stable fluoride complexes. Even 7 and 8 coordination number Ta fluoride complexes and polynuclear complexes, containing Ta_4F_{20} units were measured. One reaction was:

$$Ta(OH)_5 + (5\text{-}m)H^+ + nF^- = [TaF_n(OH)_m]^{5-n-m} + (5\text{-}M)H_2O, \qquad (18)$$

where n=1,.., 5

and $$TaF_5 + HF = H[TaF_6] \qquad (19)$$

In case of other acids present, mixed complexes will form, e.g. with sulfuric acid:

$$[TaF_n]^{5-n} + mHSO_4^- = [TaF_{n-m}(HSO_4)_m]^{5-n} + mF^- \qquad (20)$$

or with hydrochloric acid:

$$[TaF_n]^{5-n} + mCl^- = [TaF_{n-m}Cl_m]^{5-n} + mF^- \qquad (21)$$

The extreme stability of hydroxocomplexes are shown by the fact that the existence of stable $[NbOF_n]^{3-n}$ or $[Nb(OH)_2F_n]^{3-n}$ complexes is reported even in 10M HF solution. This behavior may explain why the desorption of these metals even with HF solution is a relatively slow process. A similar behavior of bismuth hydroxo-chloride complexes may also explain the slow washout of bismuth from sample introduction systems. Some of the most stable metal hydroxides and typical polynuclear hydroxo complexes, polyacids with some stability constants found in literature are summarized in Table 6.

Table 7. shows a list of stable fluoride and chloride complexes which are formed during the cleaning of surfaces with acids.

Table 8. is a brief summary of metals with a strong, moderate, and weak adsorption behavior on surfaces.

The kinetics of these complex formation phenomenon is considerably more difficult due to the barely known reaction rate constants of different complex forms. However, there is experimental proof that these reactions may be very slow, and practically complete conversion, especially to the higher ligand number complexes, may take several hours at room temperature [7,22,23,28]. These reaction rates depend on pH, temperature and the component concentrations. For illustration, see Figure 12, the rate of complexation of aluminum by fluoride ions as a function of pH, where the reaction rate was monitored by measuring the fluoride ion concentration with fluoride ISE.

As an example for boron, the following kinetic data are known for the formation of boron-tetrafluoride from borontrifluorohydroxide:

$$BF_3(OH)^- + F^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} BF_4^- + OH^- \qquad (22)$$

$$k_1 = 0.064 + 7.35 \cdot [H^+] \quad l \cdot mol^{-1} \cdot min^{-1} \qquad (23)$$

$$k_2 = 0.0009 \ min^{-1} \qquad (24)$$

The mentioned phenomenon is even more complicated if we consider the formation and behavior of homopolyacids and heteropolyacids from metal hydroxides. The increase of acid concentration, or decrease of pH, generally increases the solubility of metal hydroxides due to the fact that protons will compete for the hydroxide ligands forming water, and metal cation species, as shown by the following example reaction:

$$Zn(OH)_2 + 2H^+ \rightharpoonup Zn^{2+} + 2OH^- \qquad (25)$$

However, the decrease of pH will also cause the oligomer formation of amphoteric or acidic metal hydroxides. It is well known that homo- and heteropolyacid formations are preferred at $pH < 6$. E.g. oligomer silicates, molybdate, stannate, etc. form, since the monomer acidic forms are more stable at alkaline pH (preferred $pH > 12$), while in acidic pH ($pH < 6$) the oligomers are the stable forms. These polyacids have extremely good complex formation properties with both metal cations and with metal and semimetal based anions. The complexing of anions is well demonstrated with the properties of molybdenic acid used for the determination of silicate, arsenate and phosphate. The complexing of the metal cations is shown by the ion exchange behavior of acidic metal oxides of Ti, Si, Al, Nb, Ta, and complex forming abilities of tantalates, vanadates, tungstanates, molibdates etc. This means, that 'adsorption' of some specific metallic forms on surfaces will have synergetic effects, i.e., accelerates the adsorption or precipitation of other metals in complexed forms on the surface. This phenomenon is positively utilized, e.g., in water cleaning with colloidal aluminum-hydroxide, since aluminumhydroxide 'adsorbes' heavy metal ions on the surface.

Therefore, those metals tend to contaminate surfaces from solutions which can easily form stable hydroxides and homopolyacids. The valent state of these metals are generally 3 (Al, B, Sb), 4 (Si, Sn), 5 (Bi, Nb, Ta), and 6 (W, Mo). These acids will strongly complex 2+ (Zn, Mg, Ca) and even 1+ charged ions (e.g. $KSb(OH)_6$).

CONCLUSIONS

The following needs to be considered when new cleaning chemistries are established. The dissolution of metals from a surface, e.g., from the wall of a reactor may be a serious form of contamination, especially if the metal can easily form polyacid structures, or if the metal dissolved from a surface was not converted into a stable complex form but remains as a hydroxide complex. These metal forms will be transported to another wall with somewhat different chemical properties and may deposit on that surface. This can be a mechanism, whereby the accumulated contamination on some solid surface of an ultrapure technological system may cause serious contamination on wafers which are to be cleaned. In all these processes, the chemical complex formation equilibria, reaction kinetics, and the rate of transport processes (e.g. diffusion rate) will play an important role. Therefore, these processes should be studied together.

Sampling of ultrapure water

Hydrolization of metal ions, oligomer hydroxide and homopolyacid formation will be the most pronounced in case of ultrapure water since water should not contain any competitive ligand to the hydroxo ligands. It seems very likely from the equilibrium constants of these reactions that larger parts of metal ions, except the alkali or alkaline earth metals, i.e., most of the transition and rare earth metals, will be deposited on plastic wall. For real ppt and sub ppt metal analysis, alternative sampling techniques should be considered taking into account the mentioned properties of metal ions. A process causing problems may often be amplified to that extent that it becomes useful: the metal ion deposition and ion exchange on plastic materials is also used to preconcentrate metal ions [25,10-17]. One alternative to the DI water sampling method for trace metals can be the application of specific ion exchange columns with strong cation or anion exchange or metal ion complexing (chelating) properties, directly connected to the DI water system with a known volume of water flowing through the columns. After that, the adsorbed, concentrated ions may be eluted with appropriate acid mixtures and may be analyzed with sensitive analytical techniques, e.g., ICP-MS. Although these columns are available and successfully used in trace metal analysis, a major problem in wide spread application is the specificity of these columns. Some can bond trace metals which easily form chelate complex. Some others are good for metals in cationic forms, while others are good for metals in anionic forms (borate, stannate, tungstanate, arsenate, chromate, etc.), but no column is available which would offer quantitative adsorption of all metals in cationic, anionic and neutral forms. A simple eluting reagent would elute all the adsorbed metal ions. Therefore, if a large variety of chemical forms of metals are to be analyzed, analysis is still a complex procedure.

Wafer cleaning

Possibly, the major mechanism of metal contamination of wafers during wet chemical cleaning (besides the direct electrochemical reduction to the silicon interface) is correlated with the homo- and heteropolyacid formations with different metals, including the surface silicate groups. The oxide formation, and emphasizing the oxide formation energy, seems to be an over simplification of the phenomena since the complex forming ability of the metal ions with hydroxide ions and with silicon homopolyacids is more important. In case of aluminum, this strong hydroxocomplex and hydroxooligomer forming ability accidently coincides with a high oxide formation energy. However, it is unlikely that aluminum would really exist in an aluminum oxide form on the wafer surface after a wet chemical cleaning. This conclusion, of course, will not apply for technologies where even traces of water is excluded and the transport mechanism of metals are different than in case of wet chemistries: e.g., contamination by metal evaporation, sputtering, ion implantation, plasma CVD, and plasma etching or high temperature thermal diffusion processes.

Successful future cleaning chemistries will rely on the understanding of the decomposition of these homo- and heteropolyacid structures with competitive complex formation reactions. The recent success of diluted HF or diluted HF:H_2O_2 chemistries is based on this feature of HF. It can dissolve and complex not only the silica film, actually braking most heteropolyacid bonds, but also metals like aluminum in Al^{3+} (forms of AlF_n^{3-n}, n=1,...6) and iron in Fe^{3+} (FeF_n^{3-n}) form, preventing the redeposition of these metals onto the surface. Since HCl used in the SC2 or HPM chemistries has similar complex forming ability with some different ions, a combination of HF:HCl:H_2O_2 should be even more effective in trace metal removal from the silicon surface. Although this combination is used for cleaning of plastic surfaces, the combined application of HF and HCl in wet chemical cleaning has not yet been reported due to surface roughness problems with silicon wafers. However, HF and HCl combination has already been successfully applied to vapor phase cleaning. The volatility of both acids make them especially suitable for vapor phase application.

SUMMARY

Experimental data reveals the most frequent type of metal adsorption process for a particular mechanism. Reactions may cause significant method errors in low level trace analysis without sufficient precaution during the sampling, sample preparation and measurement process. A very sensitive instrument is no longer sufficient, not even for ultrapure water analysis. Analytical chemical experience is also required to ensure the accuracy of data. Alternative sampling methodologies need to be considered for ultrapure water analysis.

The adsorption of metals on plastic, glass, ceramic or metal surfaces is generally not a physical adsorption process, but rather a surface complex formation in most practical cases. The form of this complexation may be ion-exchange at an active site of the surface, surface complex formation directly with the metal ions or complexing of the metal hydroxides or metal homopolyacids. This later mechanism is the most probable in the case of multivalent earth metals or rare earth metals, e.g., Al, Fe, V, Mo, W, Tl, Nb, Sn, Cd, Bi, etc. These metals may form hydroxide oligomers, homopolyacids and often heteropolyacids, which can form stable bonds with the active sites of the surface. Several of these polyacids are strong complexing ligands for some additional metals, like Ca, Mg, Zn, Ba, etc.

The electrochemical reduction or electroplating reaction mechanism can also occur in metal deposition to other metal surfaces. However, this process seems to be less frequent, since most metal surface has a thin oxide-hydroxide layer which can 'trap' trace metals.

Besides the equilibrium properties of complexes, i.e., the complex formation constants, the kinetics of these complex formation, the reaction rates of different chemical reactions are also important. These, combined with the transport processes in a closed system, will determine the time function of cleanliness of any part of a system. Ultrapure water or chemical systems can no longer be characterized only by analytical data of water or the liquid chemical.

Cleaning of surfaces from trace metallic contamination involves the decomposition of the surface metal complexes, substituting the metal ions or polyacid groups with solvent based ions or groups, e.g., with protons or hydroxide ions. For efficient new cleaning chemistries, either for cleaning silicon wafers or cleaning plastic, glass, ceramic or metal walls of reactors a good understanding of both equilibria and kinetics of chemical complex formation, electrochemical processes, and a careful evaluation of transport processes in the system is needed.

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Table 1: **Chemical analysis data by ICP-MS showing possible desorption type of contamination.**

Sample ID	Nb [ppb]	Ta [ppb]
40 ppb Standard	40.885	41.679
2 % HNO3	0.096	0.111
RBLK	0.053	0.097
A1	0.068	0.101
A2	0.025	0.063
B1	**2.186**	**1.405**
B2	0.351	0.331
C1	0.055	0.047
C2	0.024	0.037
D1	**1.893**	**2.452**
1D2	0.027	0.057
2% HNO3	0	0
40 ppb standard	39.116	38.325

Table 2: **Trace metals found on the wall of polyethylene and FEP bottles.**

Al		Fe		Cr		Ni		OTHER	
ng	atom/cm^2	ng	atom/cm^2	ng	atom/cm^2	ng	atom/cm^2	ng	atom/cm^2
2.4	34	6.2	41					Sn:0.45	1.5
3.8	52	2.4	16					Sn-C: 0.3	1
7.8	108	2.4	16					Pb-C: 0.3	0.6
3	41	10.5	70.5					Zr: 0.3	1.3
3.9	56	11.1	73.7	2.9	20.8	0.8	5		
1.5	22	6.3	42	3	21.7	0.8	5		
1.5	22	8.9	59			0.7	4.5		
5	70	56	370					Cu: 0.9	5
5.7	80								

C= 1% HCl all other samples in 2% nitric acid.

Table 3.1: Trace metals on the wall of different bottles.

Bottle/Solution	Reagent	Al [ng]	Fe [ng]	Sn [ng]	Pb [ng]
T1: 0.4 ppb Group I + 0.001% nitric acid in FEP bottle	N	<0.1	<0.1	**2.1**	0.16
	C	0.7	0.9	**4.5**	0.22
	F	13	<10	**29.5**	<0.1
	Sol. ppb	0.335		**0.25**	0.328
	% Sol.	83.7		**62.5**	82
T2: 2 ppb Group I + 0.005% nitric acid in FEP bottle	N	<0.1	<0.1	**2.1**	0.07
	C	<0.1	0.7	**3**	<0.1
	F	0.7	<10	**141**	<0.1
	Sol. ppb	1.786		**1.44**	1.79
	% Sol.	89		**72**	89.5
T3: 2 ppb Group I + 0.005% nitric acid in PE bottle	N	<0.1	<0.1	**1.88**	<0.01
	C	0.4	<0.1	**4.05**	<0.1
	F	<0.1	<10	**112**	<0.1
	Sol. ppb	1.928		**1.61**	1.95
	% Sol.	96.4		**80.5**	97.5
T4: 2 ppb Group I + 0.005% nitric acid + 0.2 g ammonium citrate	N	<0.1	<0.1	**<0.1**	0.19
	C	0.24	<0.1	**<3**	<0.1
	F	2.75	<10	**<0.1**	<0.1
T8: 8 ppb Group I fresh standard with 0.02% nitric acid	N	0.15	<0.1	**1**	<0.01
	C	0.3	<0.1	**9.7**	0.14
	F	0.1	<10	**29**	<0.1

Solution IDs: N = 2 % nitric acid, C= 1% HCl, F = 1 % HF

Sol. ppb: Solution concentration before the bottles were emptied, compared to the freshly prepared 8 ppb standard as 100%.

% Sol.: The percentage of the measured concentration compared to the prepared concentration in the solution.

Table 3.2: Trace metals on the wall of different bottles.

Bottle ID:	Reagent	Nb [ng]	Ta [ng]	Bi [ng]	Pd [ng]
T5: 2 ppb Group II + 0.005% nitric acid, FEP bottle	N	0.72	0.93	5.1	1.8
	C	0.93	1.6	14.2	0.86
	F	172	231	22	1.35
	Sol. ppb	**1.4**	**1.1**	**1.67**	**1.76**
	% Sol.	**70**	**55**	**83.5**	**88**
T6: 2 ppb Group II + 0.005% nitric acid, PE bottle	N	0.6	0.29	17	1.65
	C	0.93	0.99	37	0.99
	F	291	390	47	1.1
	Sol. ppb	**1.22**	**0.75**	**1.59**	**1.78**
	% Sol.	**61**	**37.5**	**79.5**	**89**
T7: 2 ppb Group II + 0.005% nitric acid + 0.2 g ammonium citrate, PE bottle	N	<0.02	<0.1	0.42	3.44
	C	<0.02	<0.1	<2	1.08
	F	7.1	11.8	<2	0.63
T9: Fresh 8 ppb Group II + 0.02 % niric acid	N	0.1	<0.1	1.1	1.43
	C	0.31	0.45	2.2	<0.2
	F	59	60	<2	0.36

Solution IDs: N = 2 % nitric acid, C= 1% HCl, F = 1 % HF

Sol. ppb: Solution concentration before the bottles were emptied, compared to the freshly prepared 8 ppb standard as 100%.

% Sol.: The percentage of the measured concentration compared to the prepared concentration in the solution.

Table 4. **Concentration of Fe and Cu in PFA blank solutions in ppb unit after acid digestion.**

Set Number of measurements	Fe Average ppb, ng	Fe STD ppb, ng	Cu Average ppb, ng	Cu STD ppb, ng
Set 1. n=15	0.392	0.54	0.253	0.235
Set 2. n=15	0.395	0.393	6.02	3.69
Set 3/1. n=10	0.456	0.462	3.00	1.33
Set 3/2. n=12	0.433	0.397	4.84	2.03
Set 3/3 . n=10	0.616	0.609	2.59	1.87
Set 4 n=10	<0.1	0.039	0.54	0.223

Set 4. was soaked in ultrapure 1:1:2 HF:HCl:H_2O for 5 month before preparing the digestion dish blank.

Table 5: **Surface concentration of trace metals in 10^{10} atoms/cm^2 unit, after dipping into a 650 ppb metal contaminated SC1 solution and rinsed with DI water**

WAFER:	Al	Fe	Sn	Pb
Wafer #1	15,200	97	331	8.3
Wafer #2	18,600	171	330	7.5
Wafer #3 into solution with 1g/L citric acid and 1 g/L tartaric acid	15,900	11	41.5	4.1

Table 6.1: **Hydroxides, oxoacids, homopolyacids of some common metals and some formation constants.**

Metal Ions	Hydroxides, Mononuclear hydroxo complexes, Solubility Products $L=OH^-$ K_{so} , β , K_i	Polynuclear hydroxide complexes and oxo anions
Nb^{5+}		$Nb_6O_{19}^{8-}$, e.g.: $Na_7HNb_6O_{19}(H_2O)_{15,\,s}$ $Nb_{24}O_{65}^{10-}$, $H_xNb_{12}O_{37}^{(14-x)-}$
Ta^{5+}		$Ta_6O_{19}^{8-}$, e.g. $K_8Ta_6O_{19}(H_2O)_{16,\,s}$, $Ta_5O_{16}^{7-}$
Tl^{3+}	TlL_n K_1:15.7, β_2: 29-30.7; β_3, K_{so}: 38	
Sb^{3+}	SbL_3: 41.4	
Sb^{5+}		$H_2SbO_4^-$, $Sb_3O_{10}^{5-}$, $Sb_4O_{13}^{6-}$, $HSb_6O_{17}^{3-}$ $6Sb(OH)_6+3H^+ \rightarrow HSb_6O_{17}^{3-}+19H_2O$ K: 22
Bi^{3+}	BiL_3: 31, BiL_4, $BiOL_3^{3+}$,	Bi_6L_{12}: β: 168.3, $Bi_2L_2^{4+}$, Bi_9L_{20}: β 277, $Bi_2L_2^{4+}$, Bi_6L_x and $Bi_{12}L_x$ groups,

K_{so} =log K_{so} solubility product, β =log β the overall stability constant
K_i = log K_i successive stability constant [7,24-26]

Table 6.2: **Hydroxides, oxoacids, homopolyacids of some common metals and some formation constants.**

Metal Ions	Hydroxides, Mononuclear hydroxo complexes, Solubility Products $L=OH^-$ K_{so} , β , K_i	Polynuclear hydroxo complexes
Al^{3+}	AlL_3: 17.3-17.5 and 31-34 AlL_4^- β: 33.3	AlnL(3n+1)- , Al2L5+: β 33.3; Al_6L1_5: β 163, $Al_8L_{20}^{4+}$, $Al_2L_{10}^{4-}$, $Al_{2n}L^{n+}{}_{5n}$, $Al_nL_{(4n+2)}^{(n+2)-}$ n=40-100
Fe^{3+}	FeL_3: 36-39 FeL^{2+}: β 1	$Fe_2L_3^{3+}$, $Fe_3L_2^{7+}$, $Fe_2L_2^{2+}$ β 25.1
Fe^{2+}	FeL_2:12.5 -14	
Sn^{2+}	SnL : K_1 10-12	Sn_2L_2: 23.5
Sn^{4+}	SnL_6^{2-} K_1: 36.5, β_2: 41.6, β_4: 51.4, β_5: 54.6, β_6: 57.6	
Ni^{2+}	NiL: 4.6,	
Mn^{2+}	MnL: 3.4,	
Cu^{2+}	CuL: 6.1, CuL_2 β_2:13.2	Cu_2L_2; β_{22}: 17.1, β_{43}: 34
Pb^{2+}	PbL: 6.2, PbL_2: 16-20, PbL_3:13.3	
Pb^{4+}	PbL_4: 66, PbL_6^{2-}	Pb_4L_4: 36-37, Pb_6L_8: 69.3, $Pb_3L_4^{2+}$, Pb_6L_8,
Zn^{2+}	ZnL: 4.9, ZnL_2: 8.2	Zn_2L_6: 26.8

K_{so} =log K_{so} solubility product, β =log β the overall stability constant
K_i = log K_i successive stability constant [7,24-26]

Table 7: Cloride and fluoride complexes of some metals and some formation constants.

Metal Ions	Fluoride Complexes $L=F^-$, log β	Chloride complexes. $L=Cl^-$, log β	Polynuclear complexes and mixed ligand complexes
Al^{3+}	AlL_x, $x=1$-6, β_1:6.16, β_2:11.2, β_3:15.1, β_4:17.8, β_5:19.2, β_6: 19-21	AlL_4 β: 3.04	$Al_2L_7^-$ β:2.95
Fe^{3+}	FeL: 5.21, FeL_2: 9.16, FeL_3: 12, K_4:2.0, K_5:0.36, K_3:-0.3	FeL: 0.76, FeL_2: 1.06, FeL_3: 1.0, H_3FeL_6, K_1: 4, K_2: 3	
Sn^{2+}	SnL_x: K_1: 5-6, β_2:8.76, β_3: 9.25	SnL: 1.15, SnL_2:1.7, SnL_3: 1.68	
Sn^{4+}	SnL_6: 25	SnL_6^{2-}, K_1: 0.62, K_2: 0.76 K_3: 0.71, K_4: 0.33, K_5: 0.39	
Pb^{2+}	PbL: <0.3, PbL_2: K_{so}:7.57	PbL1.6,$PbL_2$1.8,$PbL_3$1.7,$PbL_4$1.4	
Zn^{2+}	ZnL: 0.73-1.5	ZnL: -0.72, ZnL_2: -0.85, ZnL_3: -1.50, ZnL_4: -1.75	
Nb^{5+}	**NbL_x $x=1$-9**, K_1:7.12, K_3:3.8, K_4:4.3, K_5: 4.5, K_6: 4.7, K_8: 3,K_9:4,	$Nb_6L_{12}^{2+}$,	$\beta(Nb(OH)_2F_4^-,F^-)$: 2.5, NbO_2Cl, $(NbCl_4)F_4$ rings, $Nb(OH)_3F_2$, $NbOCl_5^-$, Nb_2Cl_{10}, $Nb_6Cl_{28}^{4-}$
Ta^{5+}	TaL_x $x=1$-8, K_1:6.4, β_2: 11.9, β_3: 16, β_4: 19.6, β_5: 23, β_7: 30.2	$Ta_6Cl_{12}^{2+}$	$Ta_6Cl_{12}^{2+}$, $TaCl_nF^-$, $Ta_4F_4Cl_{16}$ $TaOF_6^{3-}$ Ta_4F_{20} units.
Tl^{5+}	$K_n<4$ $(n=1,2)$	TlL: 6.25, TlL_2: 11.4, TlL_3: 14.5, TlL_4: 17, TlL_5: 19.15	
Sb^{3+}	SbL_x: K_1:3, β_2:5.7, β_3: 8.3, β_4:11		$Sb_2F_7^-$, SbF_5OH^-
Bi^{3+}	BiL_x: K_1: 1.41, β_2: 0.3, β_3: 2.7	BiL: 2.4, BiL_2: 3.5, BiL_3: 5.4-6, BiL_4: 6.1-6.8, BiL_5:5.3- 6.7, BiL_6: 6.6,	

K_{so} =log K_{so} solubility product, β =log β the overall stability constant
K_i = log K_i successive stability constant [7,24-26]

Table 8: **List of metals with strong, moderate and weak adsorption properties from solutions of their ionic forms.**

Category	METALS
Metals with strong adsorption character on most surfaces: plastic, glass, ceramics.	Nb, Ta, Bi, Cd, Sn, Tl, La, Pb, Pd, W, Hg, Mo, Ir, Lu, Tm, most lantanides Noble metals, adsorption in metallic form: Hg, Au, Pt, Ag,
Very strong surface bond on silicon surface	Al, Fe, Sn
Moderate adsorption character on most surfaces: plastic, glass ceramics	Al, Fe, Sn, Cu, Ni, V, Cr, Mn, Co, Zn, Ga, Ge, Cd, Zr, In, Rh, Ru, Sc, U, Th, Ti, Y, Tb
Weak adsorption character on plastic surface	Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba

Figure 1: Adsorption and desorption of different metals in ICP-MS

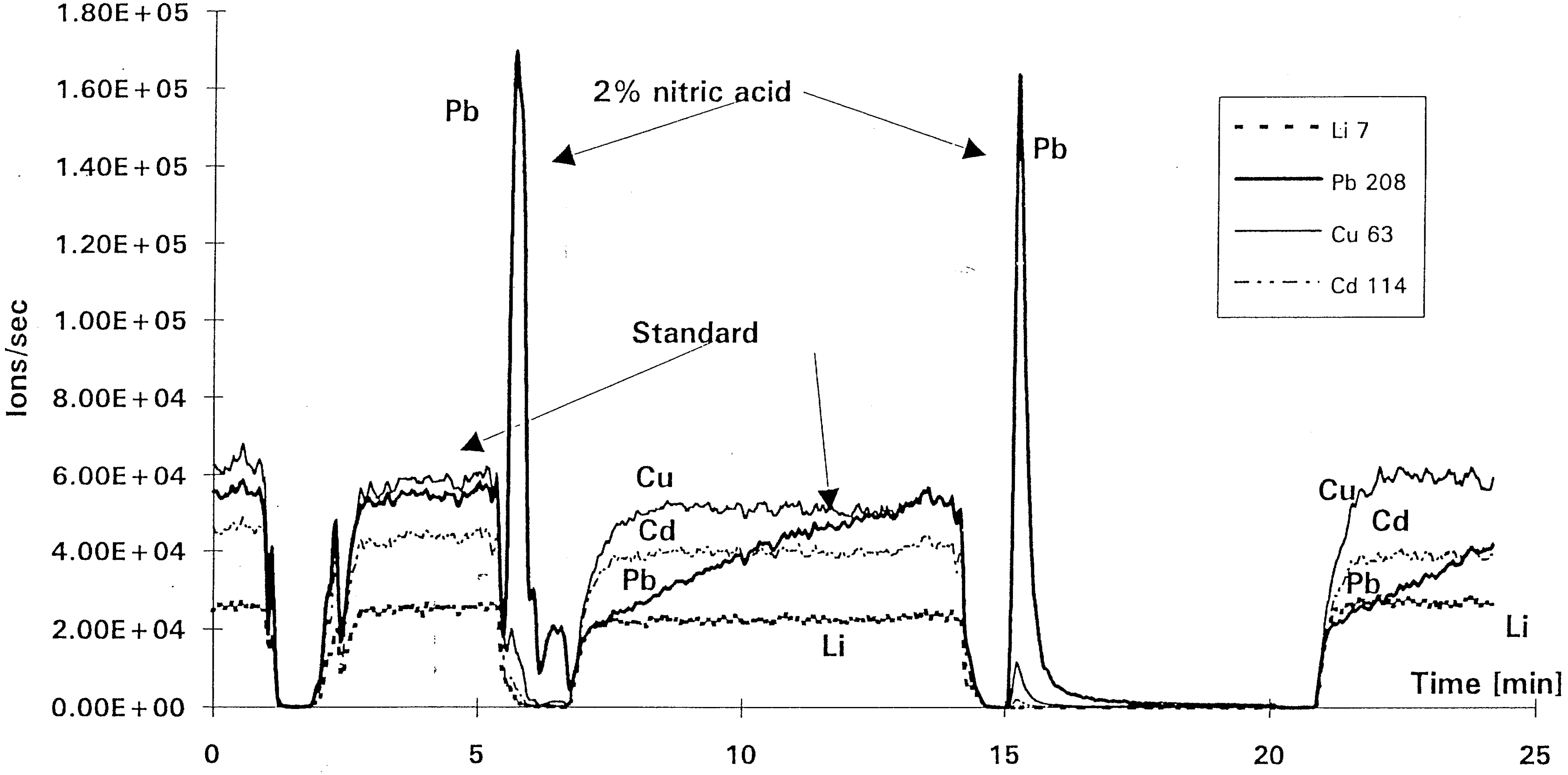


Figure 1b. Transient ion signal with acid rinse in USN

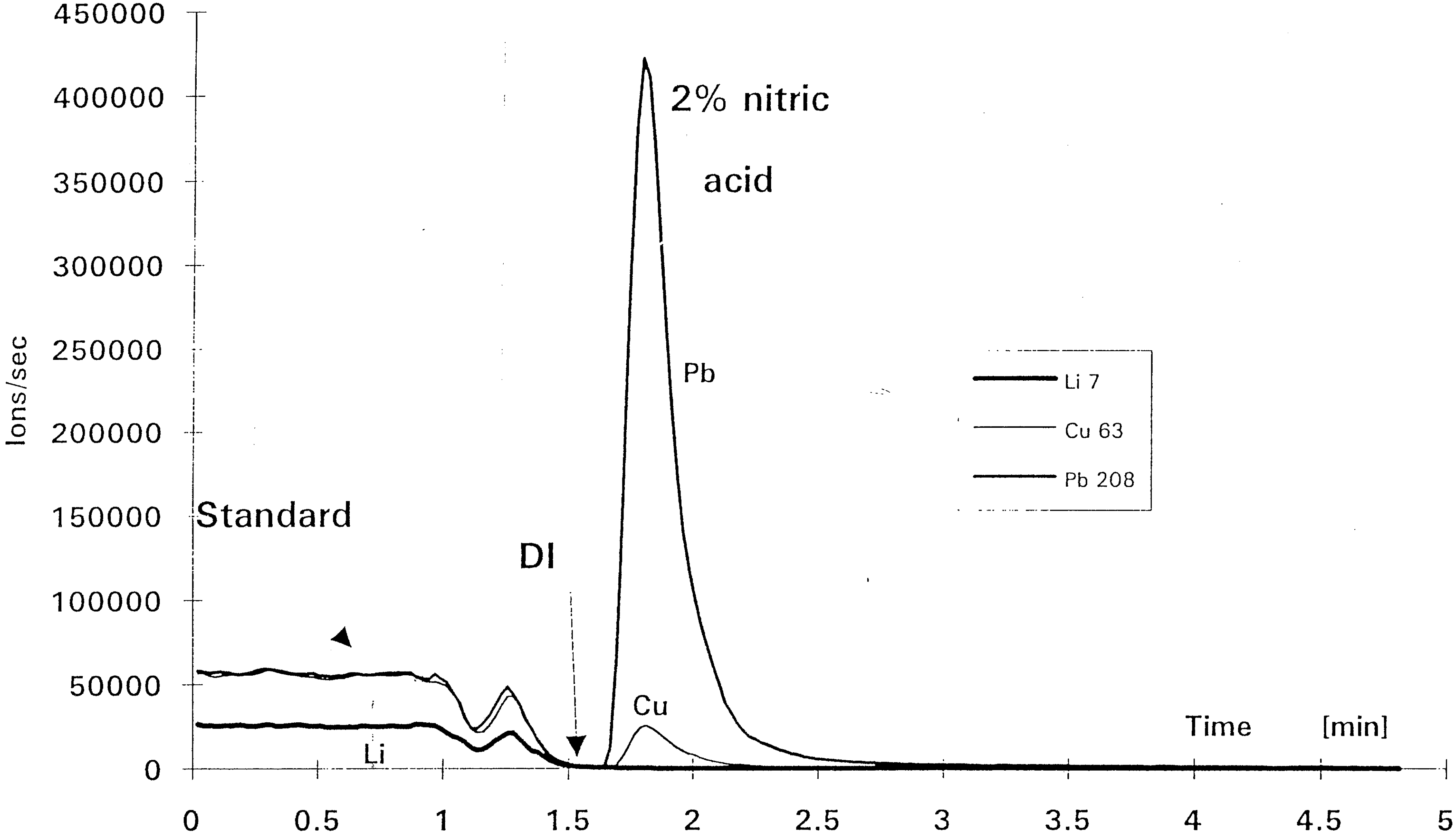


Figure 2: Metal Desorption in USN-ICP-MS with acids

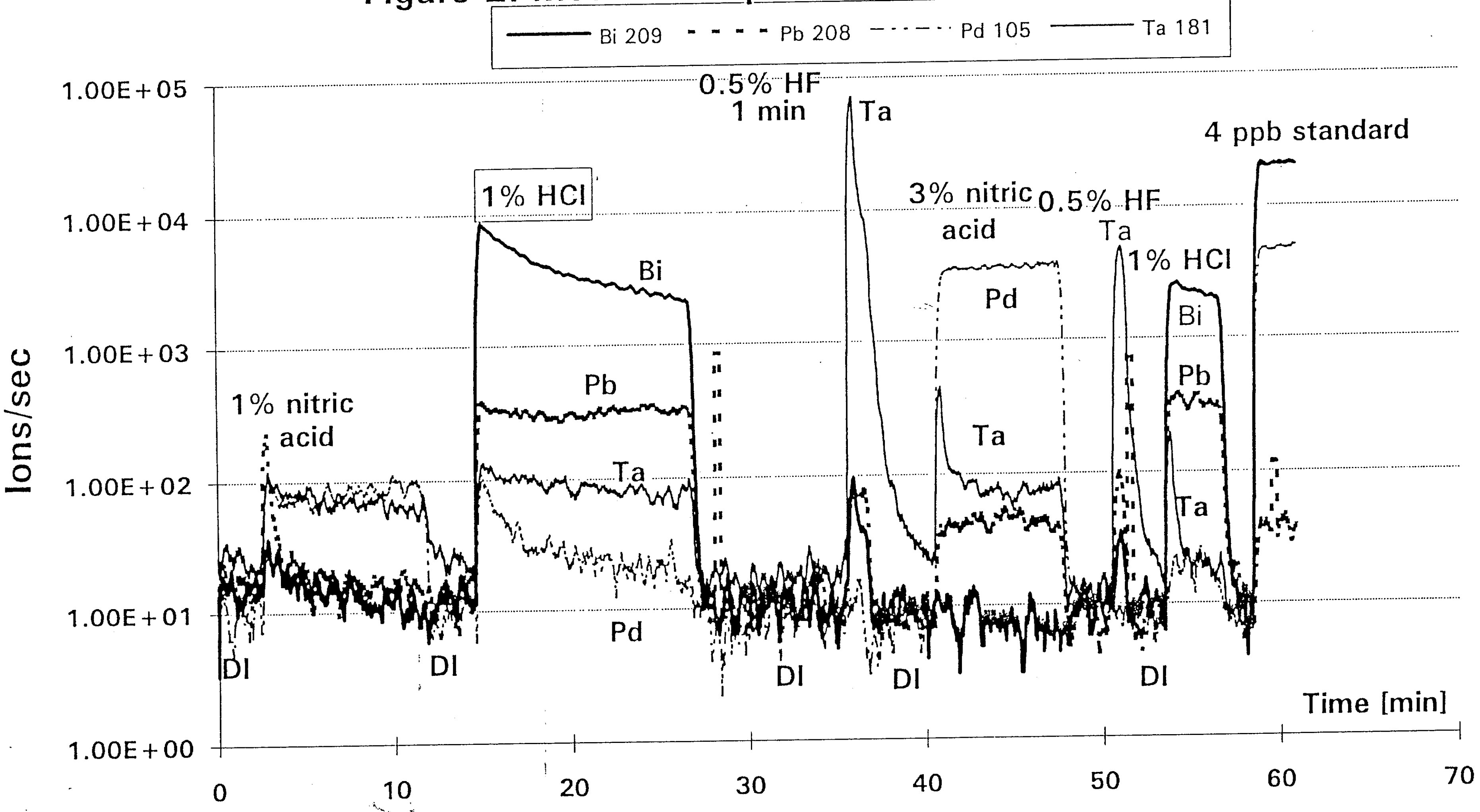


Figure 3: Desorption of Sn and Mo from USN-ICP-MS with acids

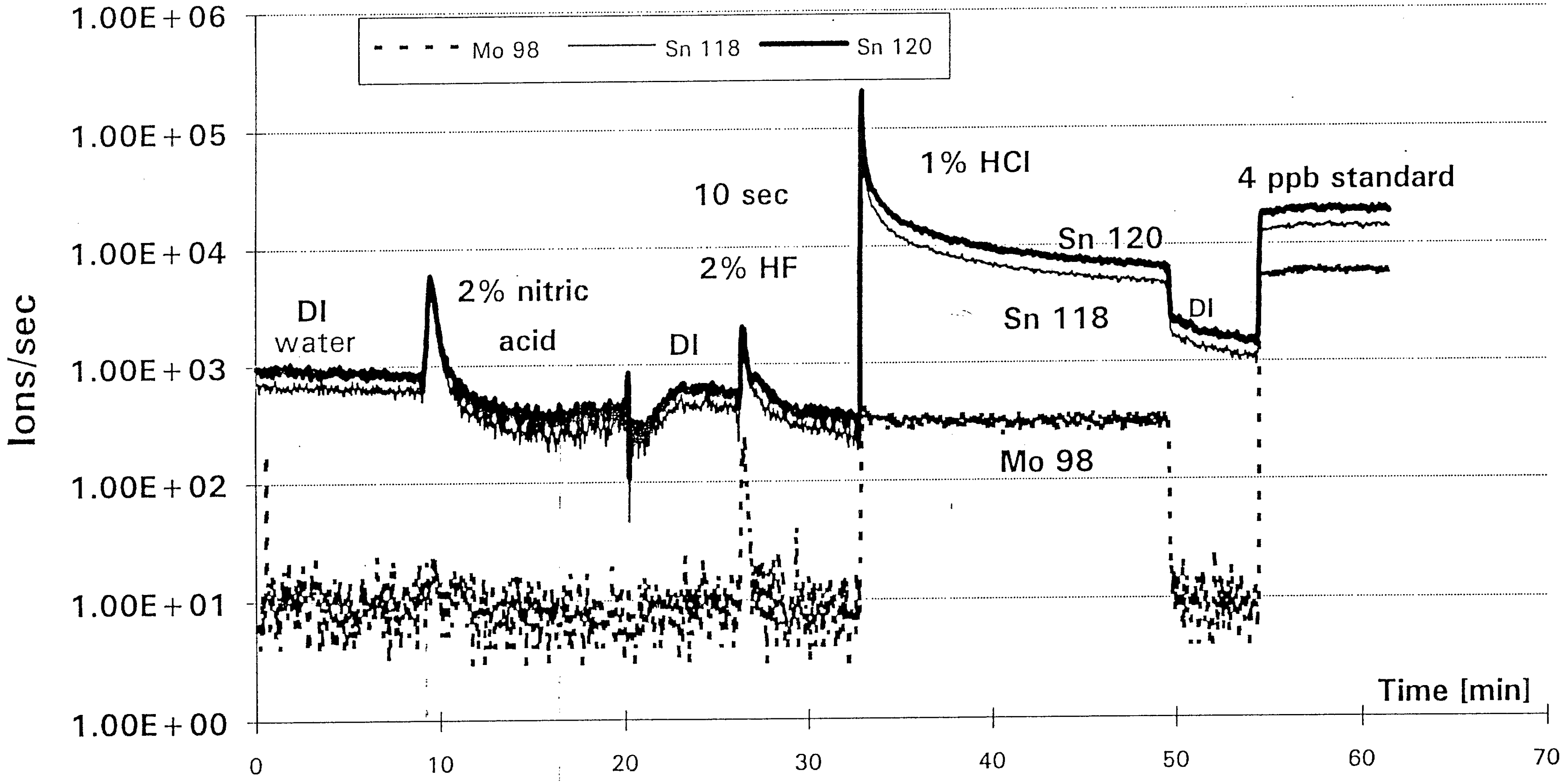


Figure 4: Injection of Sn and Cd Standard and 1 % HCl

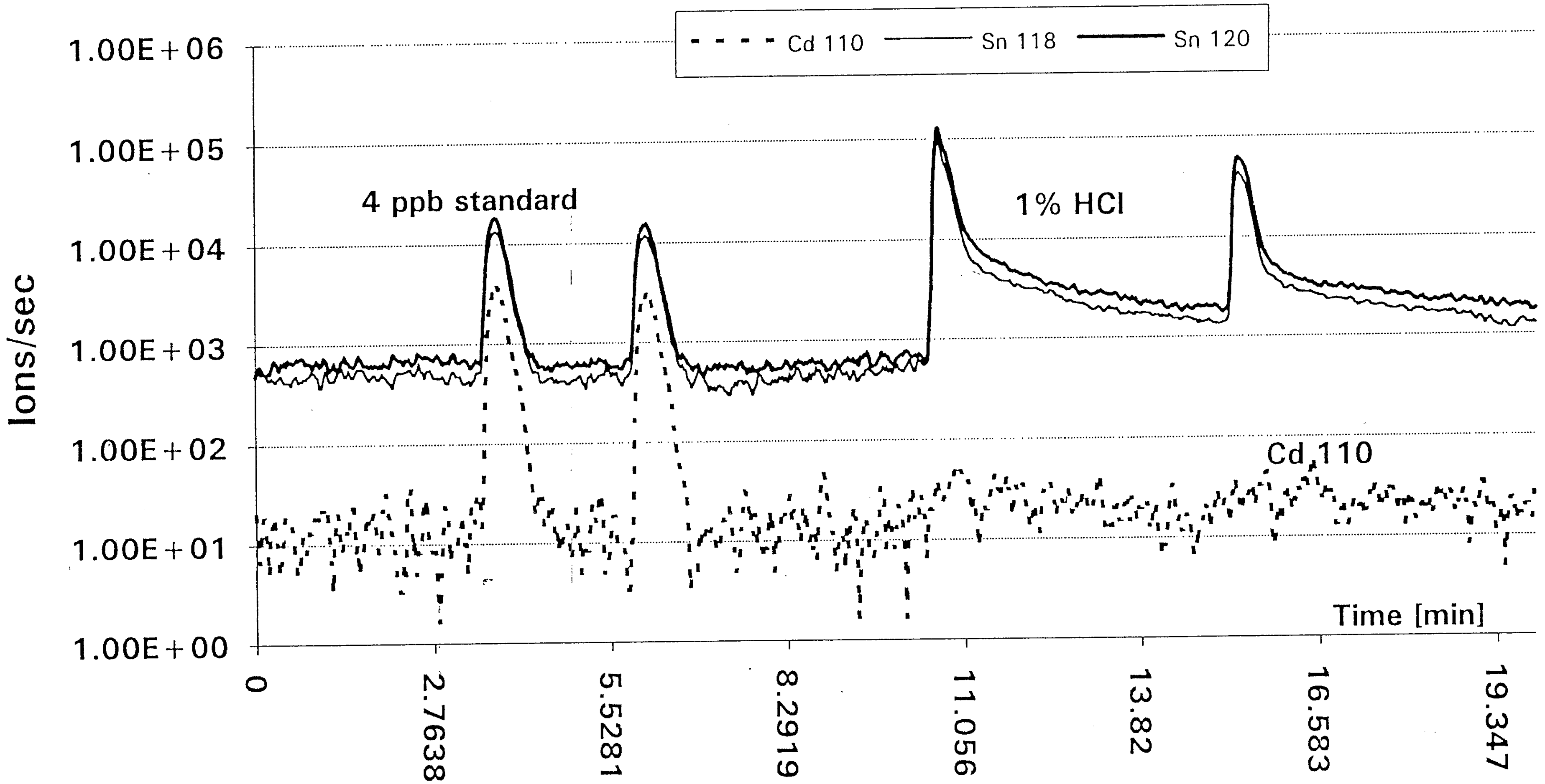


Figure 4.1: Injection of Sn and Cd Standard and 1 % HCl

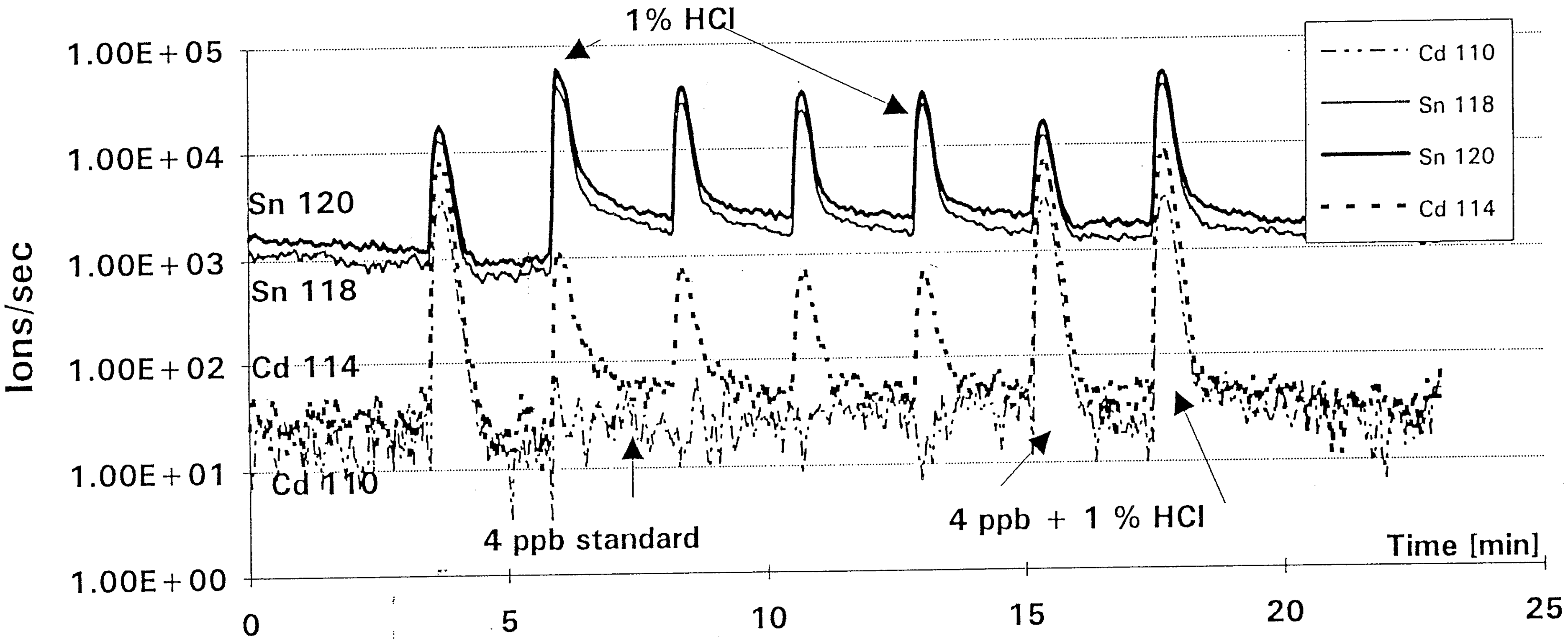


Figure 5: Desorption of metals with acids from ICP-MS with HF resistant cross-flow nebulizer and Ryton spray chamber

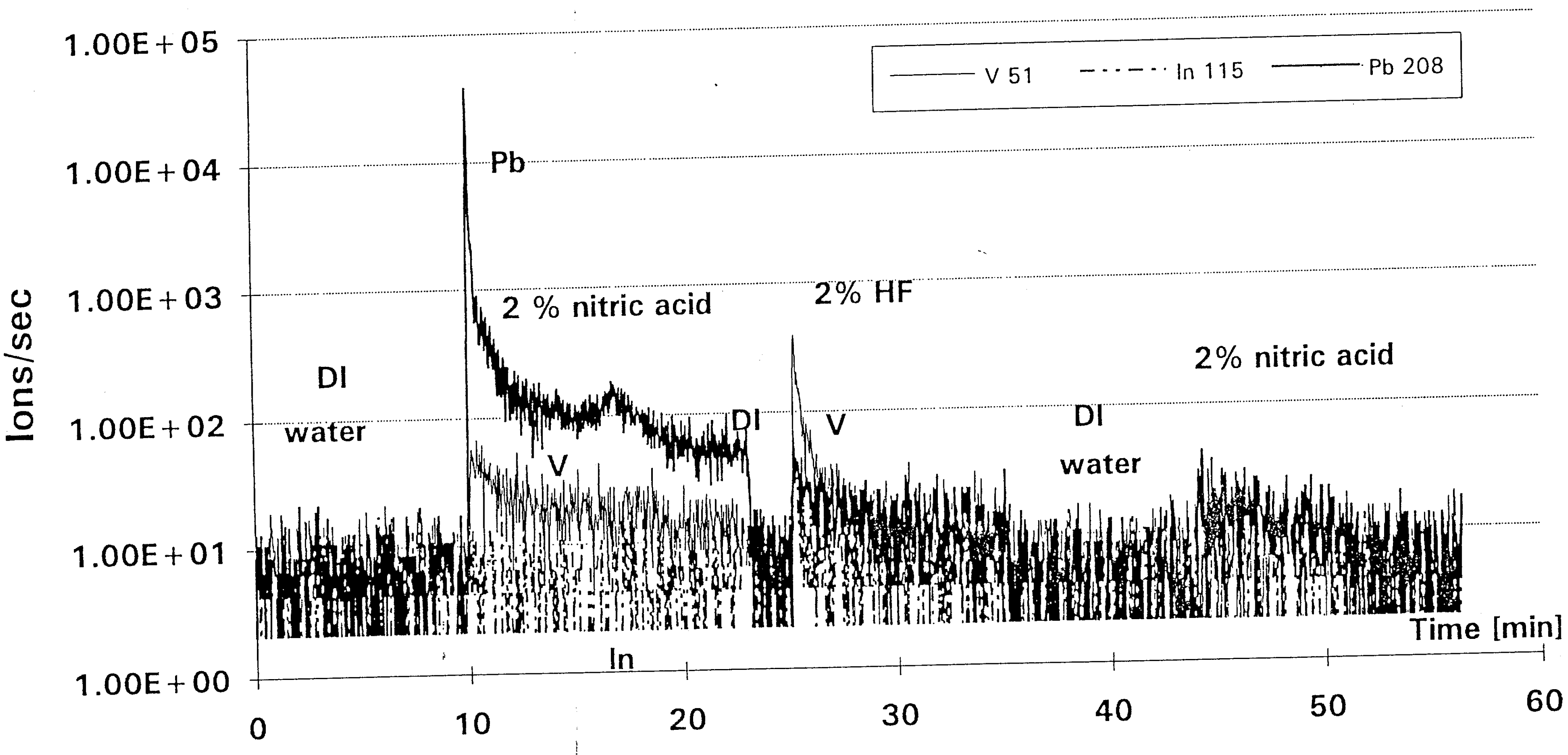


Figure 6: Desorption of Al, Mn, Co and Sn with acids from ICP-MS with Cross Flow Nebulizer and Ryton Spray Chamber

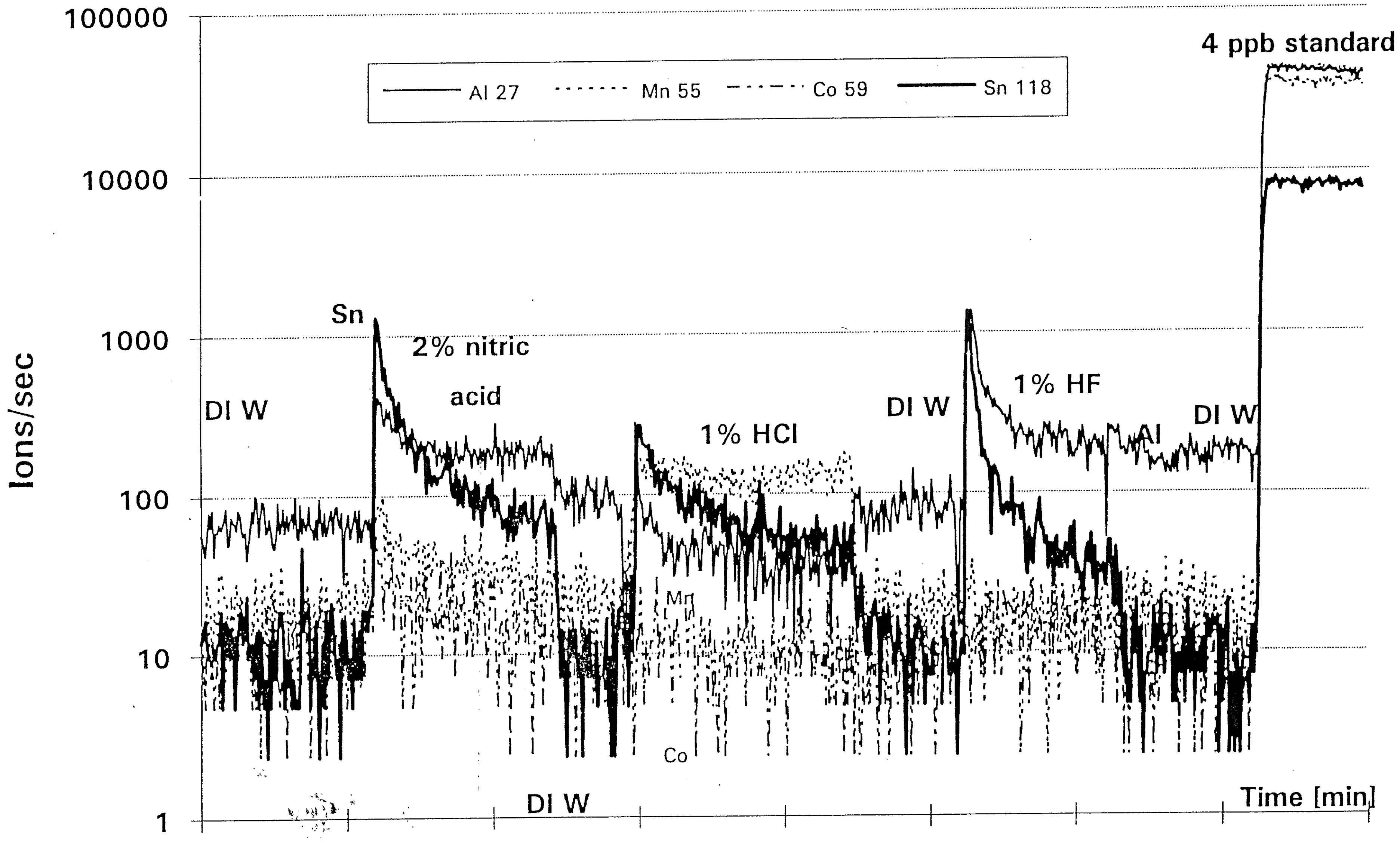


Figure 7:Desorption of Pd and La in ICP-MS with Cross Flow Nebulizer and Ryton Spray Chamber

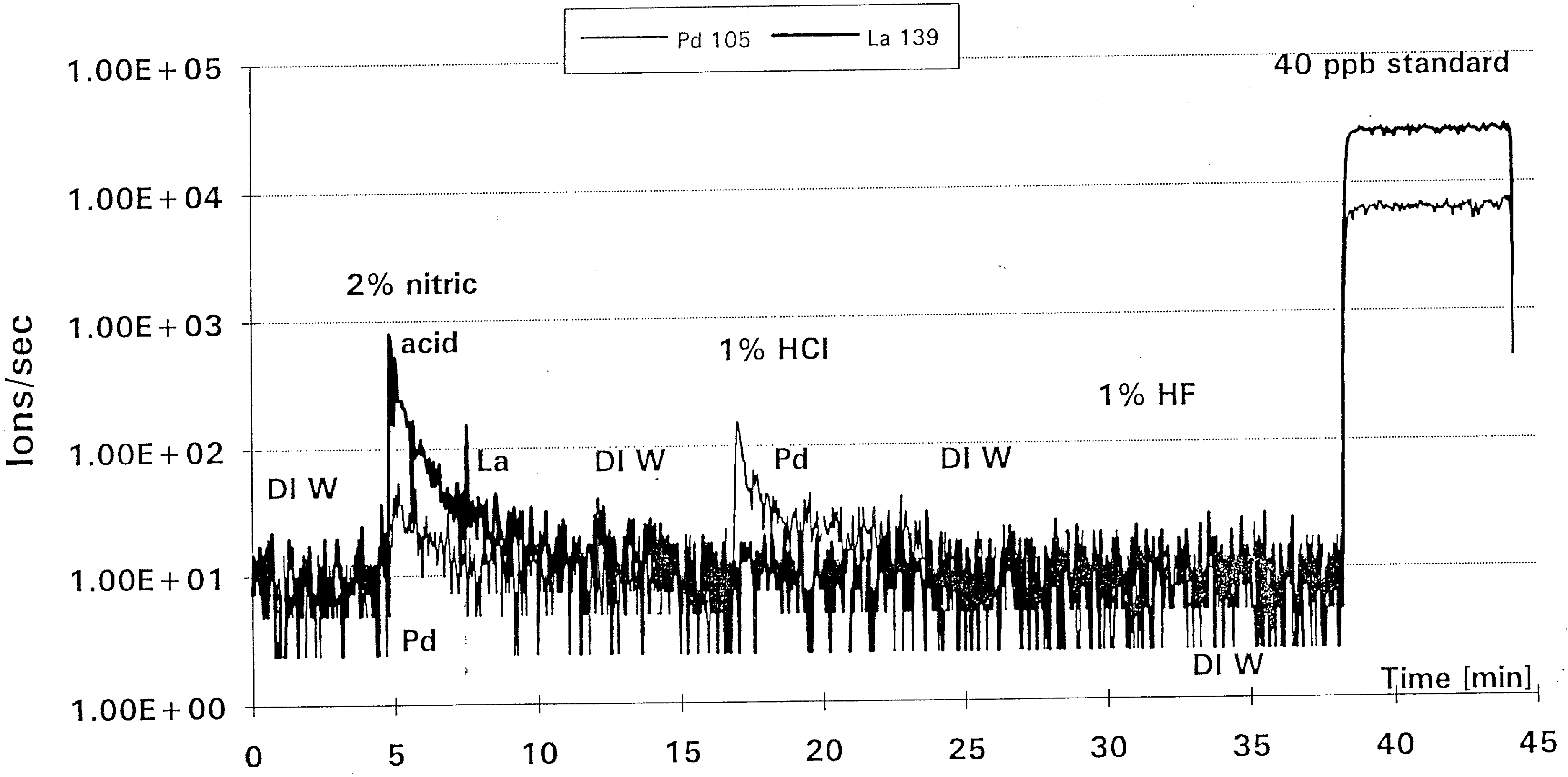


Figure 8: Desorption of Nb, Ta and Bi with acids in ICP-MS with Cross Flow Nebulizer and Ryton Spray Chamber

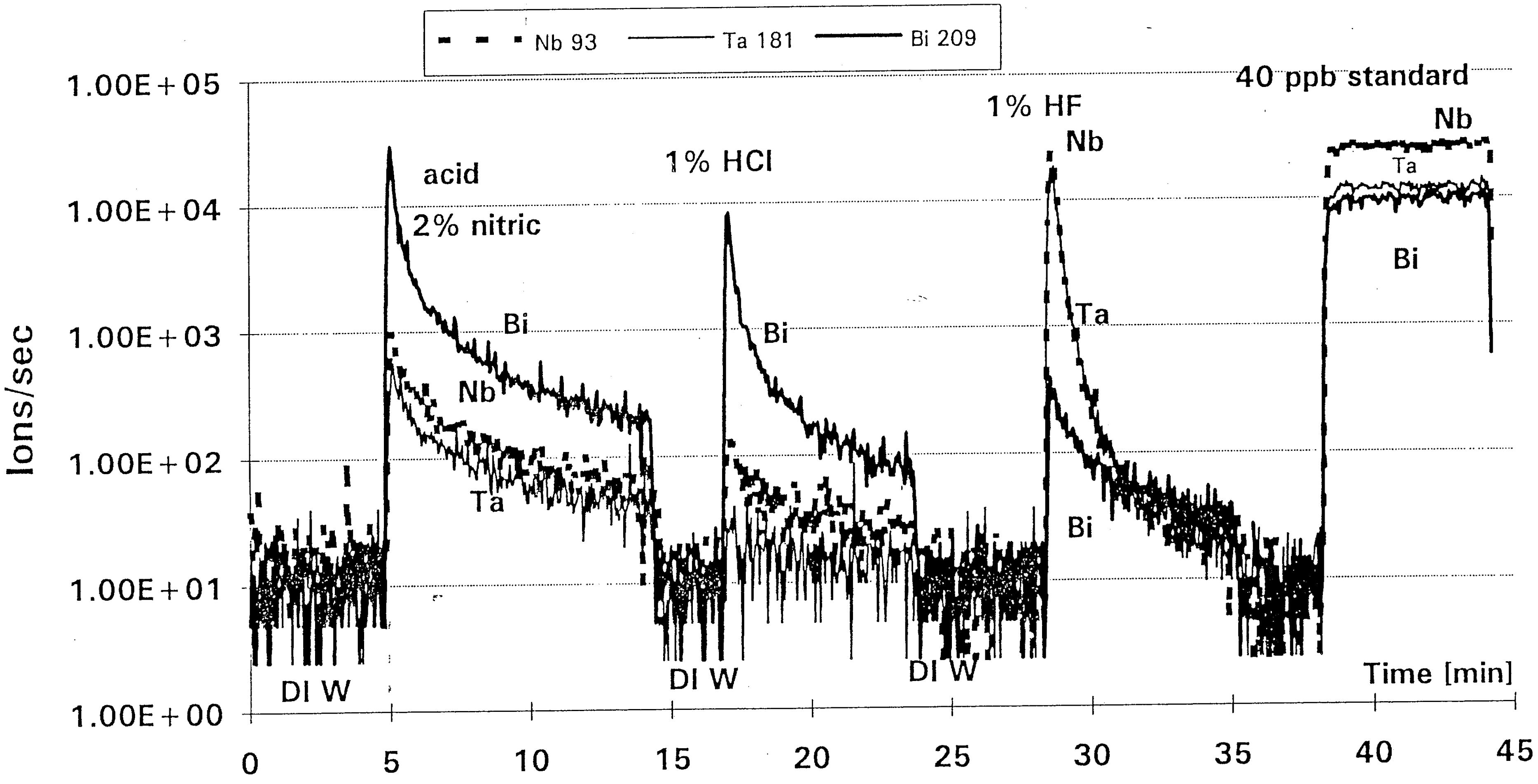


Figure 9.: Desorption of Metals with acids in ICP-MS with Meinhardt C3 Nebulizer

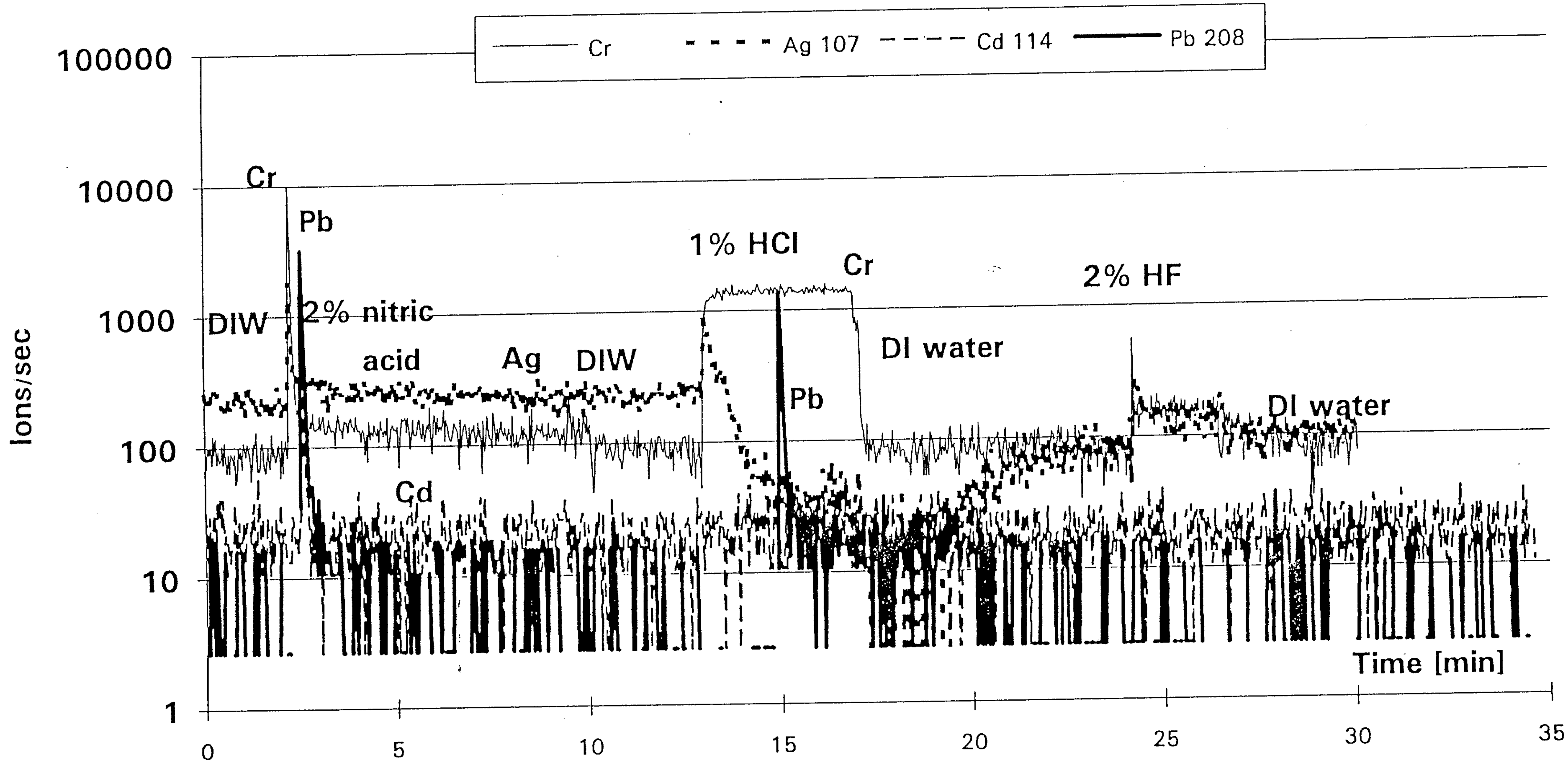


Figure 10: Different desorption rate of Bi and Sb with 1 % HCl in USN-ICP-MS system

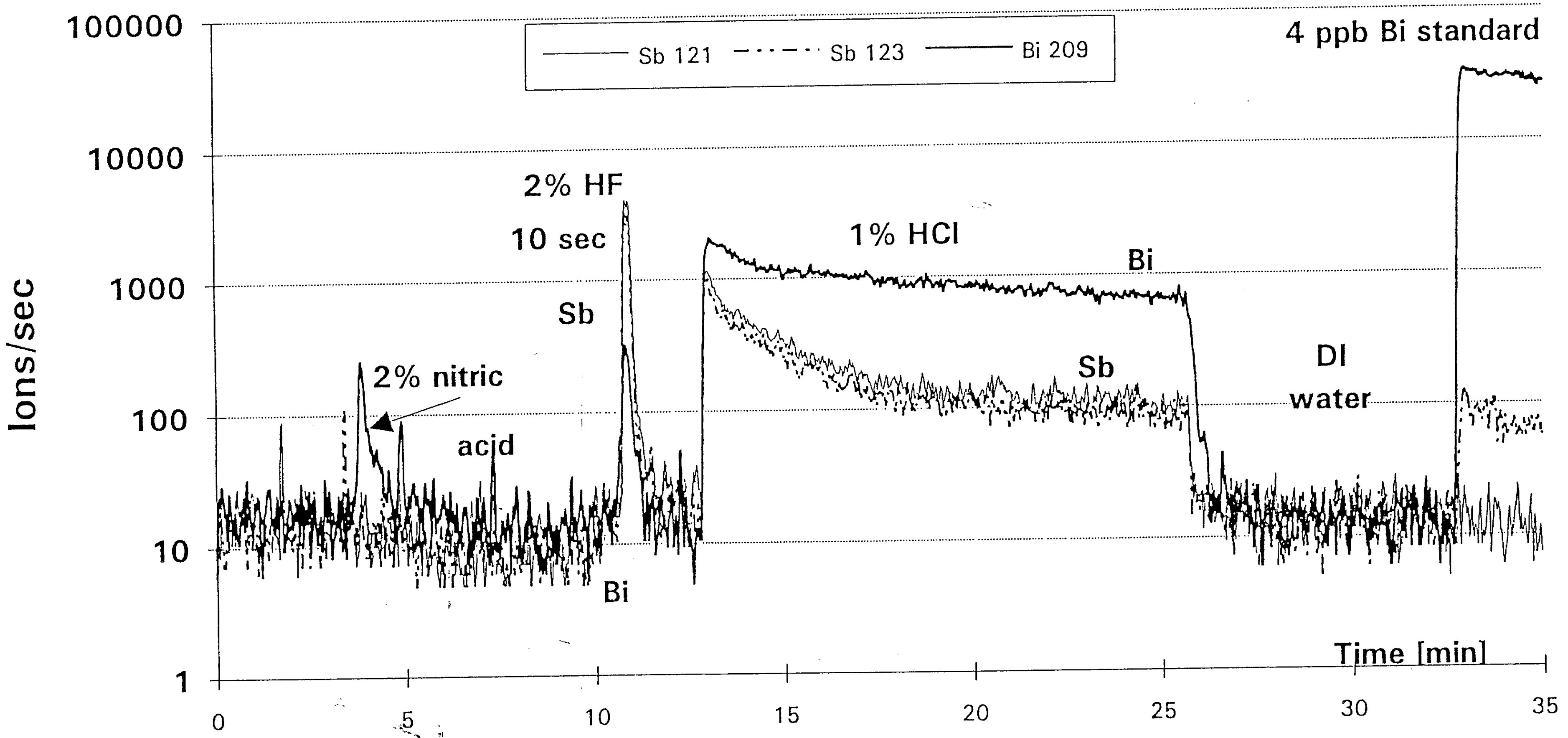


Figure 11: Injection of Sb and Bi Standard and 1 % HCl

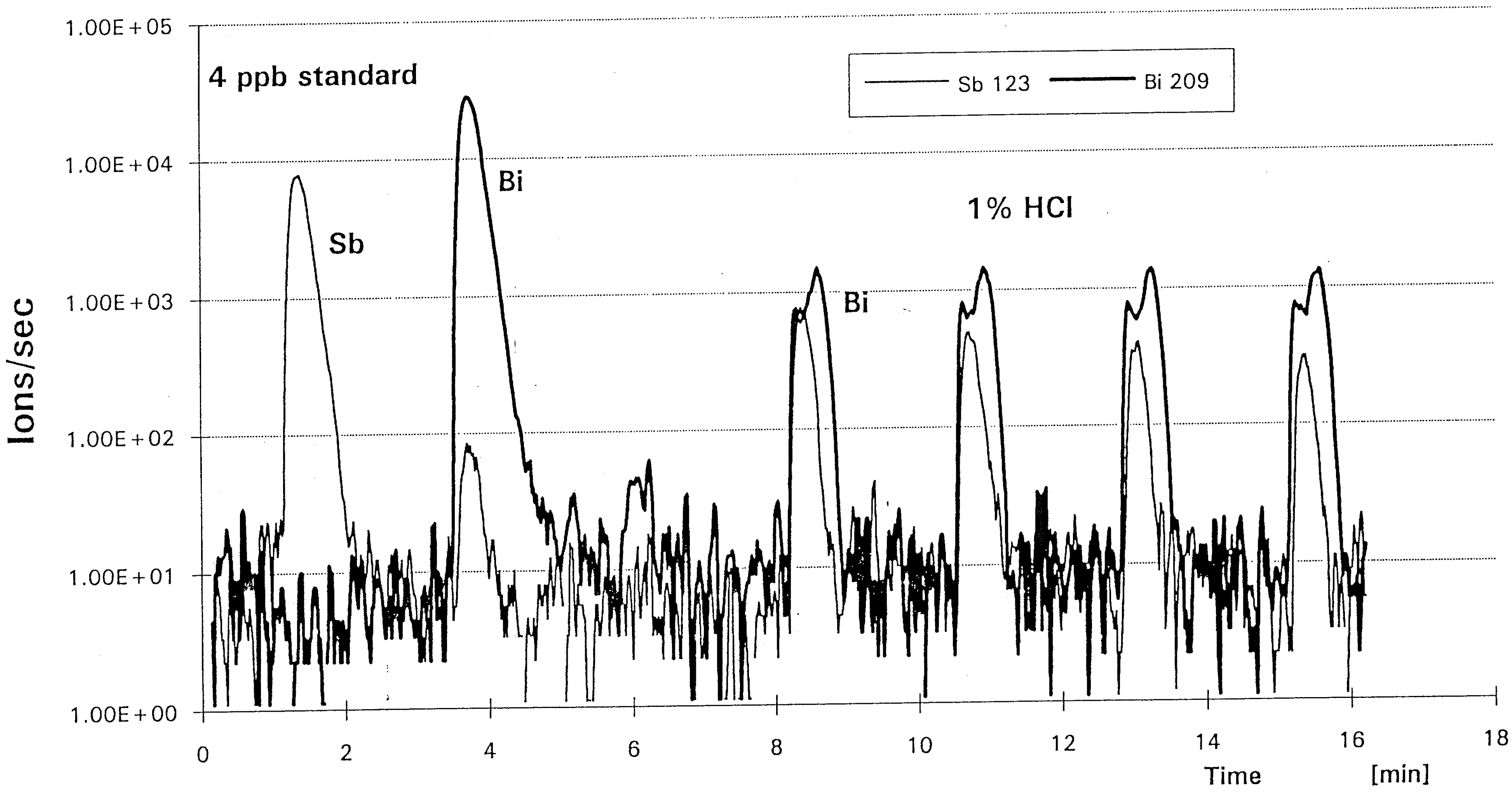
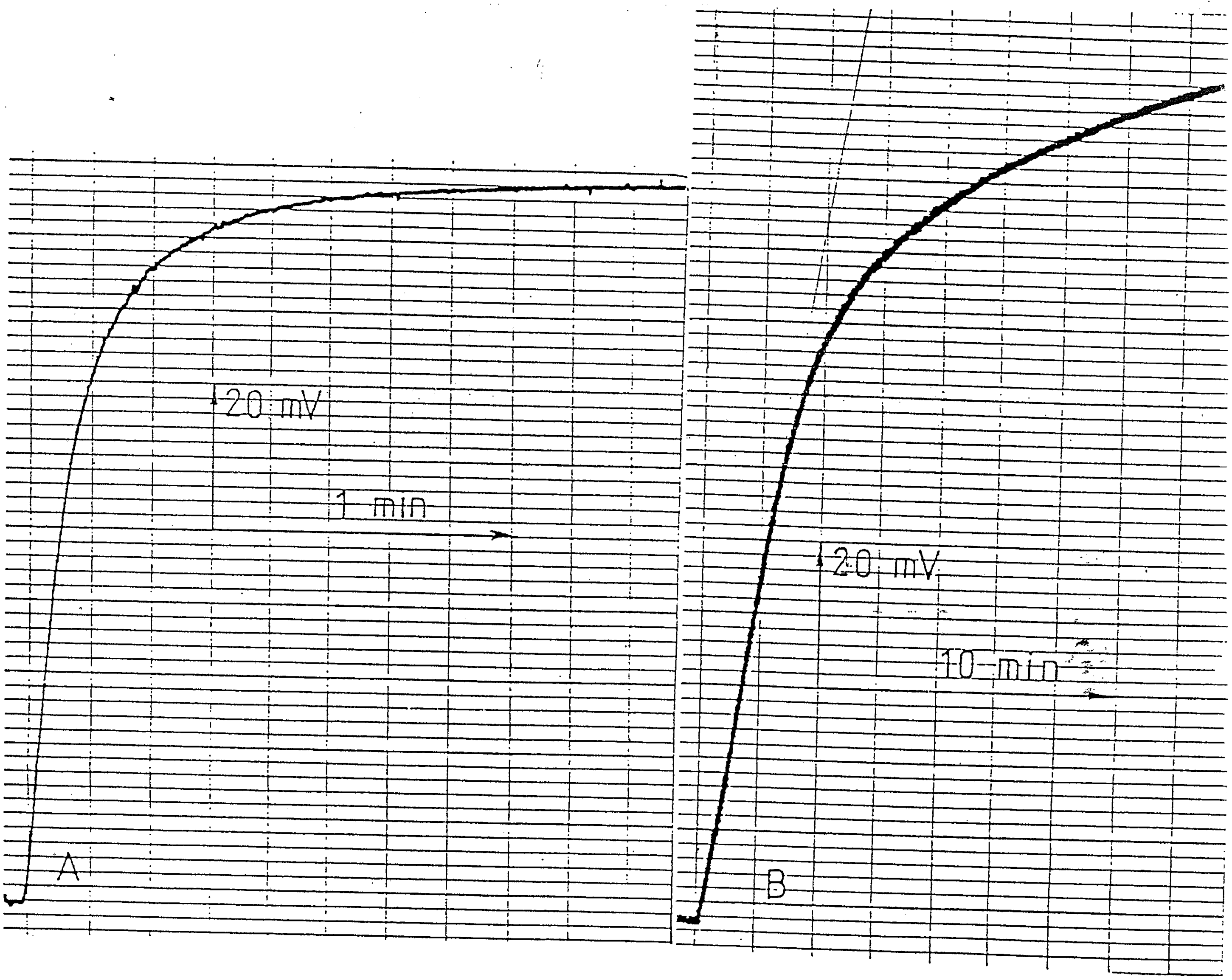


Figure 12: Complex formation kinetics: Rate of formation of aluminum-fluoride complexes. The fluoride concentration of the solution was monitored with fluoride ionselective electrodes.

A. pH=4.75 . Addition of 0.4 mL 0.1M Al^{3+}-solution into 50 mL 0.001 M fluoride solution.

B. pH=2.7 Addition of 2 mL 0.1M Al^{3+}-solution into 90 mL 0.001 M fluoride solution.



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MARJORIE K. BALAZS is the founder and president of Balazs Analytical Laboratory in Sunnyvale, CA and Austin, TX. She has worked in the Semiconductor Industry since 1968. Prior to her work in the semiconductor industry, she spent ten years at Stanford Research Institute and taught for six years at the University of San Francisco. She received her M.A. Degree in chemical education at Stanford University. She is a member of ECS, ASTM, ACS, SEMI/SEMATECH. Outstanding honors include: Award from President Reagan in 1986 as one of the 80 outstanding women entrepreneurs in the United States; 1992 City of San Jose Small Business Minority/Women Business Award; and on August 18, 1993, Ms. Balazs was honored with the 1993 SEMI Award for North America, which recognizes her contribution in yield enhancement to the semiconductor industry over the past several years.

JANOS FUCSKO, Research Chemist, joined Balazs in May 1990, and is engaged in representative research in the areas of boron on BPSG Films by ICP-MS, the development of a method for determination of trace metals in native oxide and dielectric oxide films using ICP-MS. Previously, he worked at the Hungarian Academy of Sciences in the Electroanalytical Research Group at the Institute of General and Analytical Chemistry, Technical University of Budapest for nine years where he was engaged in analytical chemical automation, flow injection analysis, electroanalytical sensors and monitors, and application of solution equilibria and kinetics in method developments for wet chemical analysis. He received his Ph.D. in Analytical Chemistry from the Technical University of Budapest in 1989. He has seven publications.