

Interpretation of the Interference Mechanisms Occurring in the Determination of Antimony(III) by Hydride Generation Atomic Absorption Spectrometry, Based on Normal Reduction Potentials

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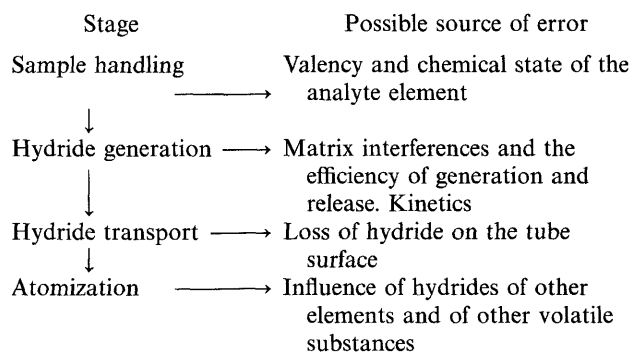
A comparative study was made of the magnitude of the interference that some chemical species produce in different inorganic acid media during the determination of Sb by hydride generation atomic absorption spectrometry (HGAAS). Differences were found in the effect of Al^{III} , Cr^{VI} , Mo^{VI} , Sn^{IV} , Ni^{II} , Co^{II} , Cu^{II} and Bi^{III} ; on the basis of these results it is possible to recommend the appropriate acidic medium for the determination of Sb by HGAAS depending on sample composition. An evaluation of interference mechanisms is also included. On the basis of results previously reported and those obtained in this work, a complete scheme, covering all the different interference mechanisms, is proposed. In particular, the use of conditional reduction potentials, and of their variation with pH, provides a basis for deducing, in a general way, whether or not a particular chemical species is capable of producing interference.

Keywords: Normal reduction potential; simultaneous interference processes; antimony determination; hydride generation atomic absorption spectrometry

A careful examination of the literature shows large discrepancies in the magnitude of the interference effects that various species provoke on Sb^{III} . According to D'Ulivo *et al.*,¹ these discrepancies are due to the action of complex mechanisms relating to the interfering species.

It is commonly accepted that the magnitude of the interference effect depends on several factors.² (1) The type of system used to generate the hydride. This could be a discontinuous, continuous or flow injection system.² (2) Chemical conditions used in the reduction process; *i.e.*, concentration and volume of the reducing agent^{3,4} or acid used.^{3,5} It is also important to consider the oxidation state of the species from which the hydride is generated.⁶ (3) The mixing order of the necessary chemical reagents.⁷ (4) The type of analysis technique used. For atomic absorption techniques, the atomization system employed is also a factor.^{8,9}

It is difficult to summarize current knowledge on the mechanisms that produce these interference effects. As a starting point, the work of Krivan¹⁰ can be used. This gives a diagram representing the stages of the hydride generation atomic absorption spectrometric (HGAAS) technique, together with the possible process types that could produce variations in the hydride readings:



Most species interfere at the hydride generation and atomization stages. Based on this, most workers^{8,11} divide the species into two groups.

(1) Elements that Normally Belong to Groups VIII (Transition Metals) and IB (Copper Group) of the Periodic Table, and which Interfere at the Generation Stage

Smith¹² was the first to investigate this subject.^{13,14} He suggested that the principal interference mechanism for this type of element was the prioritized reduction of the interfering ion to its elemental state, leading to the coprecipitation of the analyte or the absorption of the volatile hydride formed, resulting in its catalytic decomposition. Later, and in the same sense, Riby *et al.*¹⁵ found that when generating the hydride of As in the presence of Ni^{II} , the greater part of the As sample was absorbed by the precipitate of elemental Ni formed after the process.

However, other mechanisms or effects have been proposed which could explain these interferences. Meyer *et al.*,⁵ in a study of interferences on the determination of Se, proposed that after its reduction, the Se forms insoluble selenides or stable complexes in a secondary reaction with the free ions of the interfering metals. In the same way, together with Welz and Melcher,¹⁴ they showed that the kinetics of the reaction between the gas remaining at the liquid phase and the solid formed depended only on the speed of diffusion of the hydride at the gas-liquid interface and on the concentration of the interfering ion in the problem solution. This showed a correlation between the speed of formation of the precipitate of the interfering species and the extent of this interference.³

Meyer *et al.*⁵ also noted that the interferences do not always depend on the analyte/interfering agent relationship, nor on

the previous contact time between the potential interfering ion and the analyte: the concentration of the interfering species in solution is more important, although it has been demonstrated that this is not always the case.

After a study on the interference produced by Cu^{II} , Co^{II} and Ni^{II} in the determination of Se, Agterdenbos and Bax¹⁶ concluded that these species increased the extent of hydrolysis of the reducing agent before the hydride is generated, thus modifying the pH of the solution and leading to a reduction in the amount of Se that could be converted into hydride. Aggett and Boyes¹⁷ carried out studies on possible influences on the kinetics of the reaction, particularly regarding transition metals.

(2) Elements that are Capable of Generating Volatile Hydrides, such as Pb^{II} , Bi^{III} , As^{III} and As^{V} , Te^{IV} , Ge^{IV} , Se^{IV} and Sn^{II} (ref. 18)

For those species that are capable of generating hydrides, there are two causes that could explain the interference:

(i) Reactions at the liquid phase, in which the interferent could act as if it was a transition element, *i.e.*, reducing to the elemental state and decomposing, on the surface, the hydride formed.

(ii) Reactions at the gas phase, in which the interferent forms bi- or polymolecular species, with a composition yet to be determined, reducing the appearance of free atoms of the analyte.^{18,19}

The following studies were taken as a basis: those carried out by Dittrich and Mandry^{9,20} on some hydride generating elements (particularly As and Sb although extendable to other elements), by Dedina and Rubeska¹⁹ and Welz and Melcher²¹ on the atomization mechanism of arsenic hydride, and by Alkman *et al.*²² on the formation of polymeric species formed from the same analyte. From these studies, it is possible to obtain the percentage of interference that is due to the reactions in the gas phase, including the types of molecules that can be formed and how their distribution is modified by the temperature and total concentration of the element, and what percentage is due to reactions in the liquid phase.

For the determination of Sb, the results obtained to date can be summarized as follows. (i) The interference of As only occurs at low flame temperatures, owing to the formation of As–Sb species; at high temperatures there is no interference. There is no interference in the liquid phase. (ii) Interference by Bi and Se also occurs at high temperatures, which indicates the formation of bimolecular species in the flame. According to other workers,²³ there is also interference in the liquid phase during generation.

The present work presents a detailed study of the effect produced by different chemical species, possibly interferences, in the determination of Sb using the HGAAS technique. All the species used are classified according to their behaviour in the different acidic media used in the hydride generation stage: the conditions for this generation have already been established.²⁴

The objectives of this study were: (1) To determine the effect that the type of acid used in the generation has on the interference capacity of the different species studied and, therefore, to give the preferred choice in terms of the type of sample to be analysed. (2) As far as possible, to complete the diagram already proposed by Krivan,¹⁰ with new ideas about the mechanisms based on the suggestion that any particular species could interfere in more than one process. (3) To predict which species can cause an interference in the hydride results and which cannot. One of the basic reactions in the determination of an element using the hydride generation technique is an oxidation–reduction reaction, which is characterized by the value of the normal potential associated with each of the

species involved therein. The idea is to use our knowledge of these values in a simple theoretical form to make predictions. For an absolute understanding of this fact, recourse should be had, as is normal, to the values of other physical/chemical constants associated with the elements being studied.

EXPERIMENTAL

Apparatus

All measurements were performed with a Perkin-Elmer Model 2380 atomic absorption spectrometer, equipped with a hollow cathode lamp and Perkin-Elmer 056 strip-chart recorder.

The instrumental conditions used for the determination of Sb have been established previously, and the hydride generation and transport were carried out using a device described in a previous paper.²⁴

Reagents and Solutions

All chemicals were of analytical-reagent grade or better (Merck).

Concentrated acids. HCl, 1.19 g ml⁻¹, 37% m/v; HNO₃, 1.40 g ml⁻¹, 65% m/v; HClO₄, 1.53 g ml⁻¹, 60% m/v; and H₂SO₄, 1.48 g ml⁻¹, 96% m/v.

Antimony stock solution, 1000 mg l⁻¹. Prepared by dissolving potassium antimony(III) oxide tartrate hydrate in doubly distilled water.

Sodium tetrahydroborate solutions (3 and 4% m/v). Prepared immediately before use by dissolving sodium tetrahydroborate in doubly distilled water.

Solutions (2000 µg ml⁻¹) containing potential interferents were prepared from chloride or nitrate salts (for cations) and from sodium or potassium salts (for anions). In all instances working solutions were prepared by serial dilution of the stock solution with doubly distilled water immediately before use.

Procedure

In order to carry out the interference study, a series of solutions containing the same amount of Sb (3 µg) and the acid concentrations being considered were prepared, but with various amounts of added interferent. The hydride generation conditions, which depend on the acid being used, have been studied previously.²⁴

RESULTS

It is considered that a species at a given concentration does not produce interference when the variation in absorption (the absorption relative error) produced with respect to that obtained from a solution of Sb^{III} differs by less than ±10%. In terms of the results obtained, the species can be classified according to their action with the four acidic media as follows.

(1) Species whose Behaviour is Independent of the Medium

(a) Species that do not cause interference

Of the species studied, those that do not cause interference up to 2000:1 ratio (m/m) are: Li^I, Na^I, K^I, Ba^{II}, Sr^{II}, Ca^{II}, Mg^{II}, Zn^{II}, Hg^{II}(*), Cd^{II}, Mn^{II}, Sn^{II}, As^{III}, As^V, Te^{VI}, U^{VI}, Pb^{II}, Tl^I, NH₄⁺, F⁻ and Br⁻.

(b) Species that do produce interference (Table 1)

Ni^{II}, Cu^{II}, Bi^{III}, Co^{II}, I⁻ and Cr^{VI} are the species in this group. With the exception of I⁻ and Cr^{VI}, these are species that

* Analytical result not reported in this paper.

Table 1 Absorbance relative error (%)

Interfering ion	Ratio (m/m) [ion]: [Sb ^{III}]	Acidic medium			
		HCl	HNO ₃	H ₂ SO ₄	HClO ₄
Ni ^{II}	1:1	-4.0	-15.0	-17.0	-2.0
	2:1	-16.0	-29.0	-39.0	-16.0
	5:1	-43.0	-43.0	-48.0	-34.0
	25:1	-85.0	-81.0	-80.0	-77.0
Cu ^{II}	5:1	-9.0	-7.0	-1.0	-6.0
	10:1	-16.0	-21.0	-12.0	-12.0
	25:1	-22.0	-30.0	-19.0	-17.0
	100:1	-45.0	-58.0	-53.0	-43.0
	500:1	-66.0	-73.0	-66.0	-58.0
Bi ^{III}	1000:1	-77.0	-75.0	-72.0	-64.0
	5:1	-4.0	-4.0	-4.0	-4.0
	10:1	-11.0	-12.0	-25.0	-8.0
	25:1	-17.0	-11.0	-41.0	-40.0
	100:1	-36.0	-38.0	-56.0	-65.0
	500:1	-53.0	-53.0	-77.0	-72.0
CO ^{II}	1000:1	-69.0	-68.0	-87.0	-78.0
	1:1	-2.0	-2.0	-3.0	-4.0
	10:1	-1.0	-5.0	-5.0	-2.0
	50:1	-24.0	-24.0	-19.0	-29.0
Iodide	500:1	-77.0	-77.0	-76.0	-65.0
	1:1	-3.0	-10.0	-3.0	-1.0
	50:1	-8.0	-15.0	-6.0	-5.0
Cr ^{VI}	2000:1	-25.0	-30.0	-25.0	-30.0
	1:1	-24.0	-3.0	-30.0	-38.0
	50:1	-27.0	-1.0	-28.0	-38.0
Al ^{III}	100:1	-25.0	-2.0	-29.0	-39.0
	500:1	-33.0	-22.0	-30.0	-39.0
	1000:1	-50.0	-41.0	-47.0	-57.0
Sn ^{IV}	250:1	-25.0	+3.5	+3.7	-1.3
	500:1	-30.0	-5.7	-2.2	-3.2
	1000:1	-40.0	-3.2	-1.0	+3.5
	100:1	+0.5	-3.8	-1.9	-21.0
Mo ^{VI}	500:1	-8.6	-32.0	-33.0	-25.0
	1000:1	-36.0	-36.0	-34.0	-22.0
	2000:1	-44.0	-32.0	-32.0	-25.0
	25:1	-5.7	—	+4.6	—
Fe ^{III} (*)	50:1	—	—	—	-2.1
	100:1	-0.5	+23.0	-0.3	-1.2
	250:1	—	—	-12.0	-12.0
	500:1	-3.9	+13.0	-16.0	-20.0
	750:1	-32.0	—	—	—
	1000:1	-41.0	-1.3	-17.0	-22.0
	2000:1	-52.0	-17.0	-29.0	-25.0

produce a large interference effect in the hydride generation technique and which also have in common the precipitation of the elemental form during the process.

A study of the effects caused by I⁻ is of importance because of the functions that this species performs when added (in the form of KI), with or without other reagents, to eliminate possible interferences.²⁵⁻²⁷ This effect is ignored when it is used to reduce Sb^V to Sb^{III} before the hydride generation (sensitivity improvement).

(2) Species Whose Behaviour Depends on the Type of Acid Used in the Generation

Fe^{III}(*), Al^{III}, Sn^{IV} and Mo^{VI} are the species that show behaviour dependent on the type of acid, as can be seen in Table 1 where the experimental results are displayed.

DISCUSSION

A study of the possible interference mechanisms on the signal produced by antimony hydride will consider, as mentioned above, the different processes which the Sb^{III} is subjected to from the moment that the reducing agent is added until the

production of the real analytical signal. The diagram proposed by Krivan¹⁰ can be completed in the following way, with particular attention to the first two stages:

(1) Before generation, the Sb^{III} is in solution in an acidic medium.

(2) The reducing agent is added, producing the simultaneous formation of H₂ and Sb^{-III}.

(3) The hydride SbH₃ is formed.

(4) The hydride is released from the solution.

From the data already available from other workers (given in direct or indirect form) and from our own work, the substances that produce the greatest interference effect do so via one of the following mechanisms.

1. Before Generation

(1-a) Substances that produce the oxidation from Sb^{III} to Sb^V, carrying out the hydride generation from the oxidation state and obtaining lower sensitivity in the hydride signal. It is observed that in order for a species to act in this way, its normal reduction potential must be superior to that of the Sb^V-Sb^{III} system.

(1-b) Substances formed from complexes or precipitation agents, which affect the Sb^{III} to be found as such in solution. The species that interfere in this way can be predicted from their corresponding formation constants.

2. Formation of Sb^{-III} After the Addition of the Reducing Agent

(2-a) The interferent, which could be a substance with redox characteristics, reacts with the tetrahydroborate in preference to the Sb, partly consuming it. In order that a species can act in this way, one of its normal reduction potentials (acidic or basic medium) must be higher than that of the Sb^{III}-Sb^{-III} system. In fact, the concentration of interferent necessary to make the reduction in the available reducing agent noticeable must be very high. Its importance is therefore relatively low, although many workers postulate this as one of the most important processes for explaining interference.

(2-b) The fact that the hydride generation is produced from an acidic medium seems to depend only on the acidity of the solution before the addition of the reducing agent. At that moment, and together with the formation of the hydride and hydrogen, a change in the acidity of the solution is observed as it acquires a strongly basic pH owing to the acid-base characteristics of the reducing agent (hydrolysis). In the absence of other effects, it is accepted that the process of hydrolysis of the reducing agent occurs later than the hydride generation process in such a way that the evolution of the SbH₃ occurs while the medium is still acidic. Nonetheless, it has been indicated above that some chemical species are capable of accelerating or inducing the hydrolysis process, provoking an inversion in the order in which the process occurs in such a way that the hydride would be generated from a basic medium: a large decrease in the signal is then observed. In order to evaluate whether or not a given species will interfere with this mechanism the constants for the velocity of the process would have to be available: in almost every situation, they are not known.

3. Formation of the Antimony Hydride

It has been observed that some cations are able to react in a way that reduces the analyte by forming insoluble salts. The species that form the cationic part of these salts are normally elements that can also be reduced, but their reduction kinetics are slower than that of Sb. This means that, in addition to having available the corresponding solubility products, a wide knowledge of the reduction kinetics of these species is also necessary for an evaluation of their possible interference.

4. Processes Occurring after Hydride Formation

It is known that some transition elements (in a zero oxidation state) can act as catalysts in processes which involve the decomposition of organic or inorganic species. SbH_3 is an unstable species which can decompose into Sb^0 and H_2 . If we bring these concepts together and consider them in the light of point 2-a, we see that the elemental species formed as a consequence of the reductive action of the tetrahydroborate can act as catalysts for the decomposition of the hydride, thus causing reduced energy in the analytical signal received. In order for an element to be capable of interfering with this mechanism, its reduction is necessary: therefore its normal reduction potential to the elemental state must be higher than that of the $\text{Sb}^{\text{III}}\text{-Sb}^{-\text{III}}$ system. It must also have a catalytic action, which is attributed to the transition elements.

The mechanisms explained above are really basic and simple processes. Even if they permit an explanation of the interference caused by some species, they do not cover every aspect in a satisfactory way: one must postulate other mechanisms, taking as a starting point the fact that some species interfere because they are capable of affecting several of the processes indicated simultaneously.

The most likely combined mechanisms for consideration are:

(I) When a species acts to cause the oxidation of Sb^{III} to Sb^{V} (1-a), the process will lead to the appearance of a reduced form of that species, which in turn can act as a new interferent. This type of behaviour can be predicted if the successive normal potentials of the interferent species are considered simultaneously.

(II) The fact that a substance forms complexes (1-b) does not prevent it from also acting according to any of mechanisms 2, 3 or 4 mentioned above, if its interference in this sense is observed for high concentrations, which is really when the free concentration of the species is significant.

(III) The interference produced by hydrolysis (change in the acidic medium: 2-b) is not incompatible either with the idea that the species may reduce in a form preferential to the Sb reduction, producing both a consumption of reducing agent (2-a) and the possible decomposition of the hydride on its surface (4). Nonetheless, if this is so the prediction of inter-

ference should be carried out from the combined normal potentials in an alkaline medium: this can be obtained theoretically.

(IV) Finally, when the hydrolysis process occurs before Sb reduction, there is the highest probability that the $\text{Sb}^{-\text{III}}$ species could exist as such. If the solution contains a cation that either presents a very low reduction potential or one that is below that of Sb^{III} , logically in an alkaline medium, the formation of insoluble antimonides can be foreseen; we should, therefore, search amongst these species for those that could interfere in this way.

As we have seen, some of the interference mechanisms could be checked by using only the normal reduction potentials for the species studied, both in acidic and alkaline media. In order to explain the others, knowledge is required of other thermodynamic constants which are less readily accessible (*i.e.*, rate-constants, bonding).

The species studied in this work can be classified into groups, based on the normal reduction potentials for the systems corresponding to the element that is the object of the study, $\text{Sb}^{\text{V}}\text{-Sb}^{\text{III}}$ and $\text{Sb}^{\text{III}}\text{-Sb}^{-\text{III}}$, and from the viewpoint of the normal potential values of the chemical species studied (shown in Table 2). The groups are:

(1) Species whose Reduction Potential is Lower than the $\text{Sb}^{\text{III}}\text{-Sb}^{-\text{III}}$ System in an Acidic Medium. A Sub-division can be Made According to Whether this Potential is also Lower in Alkaline Media or Not

All these species are those that, in principle, should present a lower interference problem, as they are not capable of oxidizing Sb^{III} to Sb^{V} , nor of being reduced preferentially to Sb^{III} .

Of the species studied, Tl^{I} , Cd^{II} , Zn^{II} , Mn^{II} , Al^{III} , Mg^{II} , Na^{I} , Ca^{II} , Sr^{II} , Ba^{II} , K^{I} and Li^{I} belong to this group. Apart from Al^{III} , and then only in an HCl medium, none of these species produced significant variation in the Sb signal.

The interference of Al^{III} in the HCl medium can be explained by the formation of a complex with the tetrahydroborate²⁸ of formula $[\text{Al}(\text{BH}_4)_3]$.

Only Tl^{I} and Cd^{II} were reduced to the elemental state, with the observation of a metallic precipitate. It has, therefore, been shown experimentally that this reduction takes place later than the hydride generation and does not affect its free evolution.

(2) Species with a Reduction Potential Greater than that of the $\text{Sb}^{\text{V}}\text{-Sb}^{\text{III}}$ System

All the species that are found within this group can cause a partial interference to the antimony hydride signal, as they are capable of oxidizing Sb^{III} to Sb^{V} before the addition of the reducing agent and producing hydride generation from this oxidation state. The reduced form of these species can also continue to act as a new interference.

Cr^{VI} , $\text{Fe}^{\text{III}}(*)$ and $\text{Hg}^{\text{II}}(*)$ form part of this group.

Cr^{VI} produces interference (see Table 1) although increasing the dichromate concentration does not keep it constant, as could be expected. (The hydride generated from Sb^{V} gives a signal 20–50% lower than that generated from Sb^{III} .¹⁰) The signal reduction is not proportional owing to kinetic problems.

$\text{Fe}^{\text{III}}(*)$ interferes at very high concentrations, but $\text{Hg}^{\text{II}}(*)$ does not interfere at all. Both the interferent and non-interferent mechanisms have been explained in detail in a previous study.²⁹

(3) Species whose Reduction Potential is Between the Two in Acidic Media, with new Sub-divisions Depending on Whether or Not this Difference is Maintained in Basic Media

All the species belonging to this group are expected to reduce preferentially to Sb after the addition of the reducing agent. However, this preferential reduction takes place only when the

Table 2 Values of normal reduction potentials of the chemical species studied

Acidic medium		Basic medium	
E/V	Redox system	E/V	Redox system
+1.33	$\text{Cr}^{\text{VI}}\text{-Cr}^{\text{III}}$	+0.10	$\text{Hg}^{\text{II}}\text{-Hg}^0$
+0.80	$\text{Hg}^{\text{II}}\text{-Hg}^0$	-0.13	$\text{Cr}^{\text{VI}}\text{-Cr}^{\text{III}}$
+0.77	$\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$	-0.22	$\text{Cu}^{\text{II}}\text{-Cu}^0$
+0.75	$\text{Sb}^{\text{V}}\text{-Sb}^{\text{III}}$	-0.34	$\text{Tl}^{\text{I}}\text{-Tl}^0$
+0.74	$\text{Se}^{\text{IV}}\text{-Se}^0$	-0.35	$\text{Se}^{\text{IV}}\text{-Se}^0$
+0.65	$\text{Mo}^{\text{VI}}\text{-MoO}_2$	-0.46	$\text{Bi}^{\text{III}}\text{-Bi}^0$
+0.56	$\text{As}^{\text{V}}\text{-As}^{\text{III}}$	-0.54	$\text{Pb}^{\text{II}}\text{-Pb}^0$
+0.51	$\text{Mo}^{\text{VI}}\text{-Mo}^{\text{III}}$	-0.56	$\text{Fe}^{\text{III}}\text{-Fe}^{\text{II}}$
+0.47	$\text{Te}^{\text{VI}}\text{-Te}^0$	-0.57	$\text{Te}^{\text{VI}}\text{-Te}^0$
+0.34	$\text{Cu}^{\text{II}}\text{-Cu}^0$	-0.59	$\text{Sb}^{\text{V}}\text{-Sb}^{\text{III}}$
+0.33	$\text{U}^{\text{VI}}\text{-U}^{\text{IV}}$	-0.67	$\text{As}^{\text{V}}\text{-As}^{\text{III}}$
+0.32	$\text{Bi}^{\text{III}}\text{-Bi}^0$	-0.68	$\text{As}^{\text{III}}\text{-As}^0$
+0.25	$\text{As}^{\text{III}}\text{-As}^0$	-0.72	$\text{Ni}^{\text{II}}\text{-Ni}^0$
+0.15	$\text{Sn}^{\text{IV}}\text{-Sn}^{\text{II}}$	-0.73	$\text{Co}^{\text{II}}\text{-Co}^0$
-0.04	$\text{Fe}^{\text{III}}\text{-Fe}^0$	-0.78	$\text{Mo}^{\text{VI}}\text{-MoO}_2$
-0.13	$\text{Pb}^{\text{II}}\text{-Pb}^0$	-0.81	$\text{Cd}^{\text{II}}\text{-Cd}^0$
-0.14	$\text{Sn}^{\text{II}}\text{-Sn}^0$	-0.91	$\text{Sn}^{\text{II}}\text{-Sn}^0$
-0.25	$\text{Ni}^{\text{II}}\text{-Ni}^0$	-0.93	$\text{Sn}^{\text{IV}}\text{-Sn}^{\text{II}}$
-0.28	$\text{Co}^{\text{II}}\text{-Co}^0$	-1.17	$\text{Sb}^{\text{III}}\text{-SbH}_3$
-0.29	$\text{Sb}^{\text{III}}\text{-SbH}_3$	-1.23	$\text{Zn}^{\text{II}}\text{-Zn}^0$
-0.34	$\text{Tl}^{\text{I}}\text{-Tl}^0$	-1.26	$\text{As}^{\text{III}}\text{-AsH}_3$
-0.36	$\text{As}^{\text{III}}\text{-AsH}_3$	-1.44	$\text{Fe}^{\text{III}}\text{-Fe}^0$
-0.40	$\text{Cd}^{\text{II}}\text{-Cd}^0$	-1.62	$\text{U}^{\text{VI}}\text{-U}^{\text{IV}}$
-0.76	$\text{Zn}^{\text{II}}\text{-Zn}^0$		

difference between the potentials is large: a commonly accepted criterion is 0.3 V. Given this, two groups can be considered:

(3.1) Ni^{II}, Co^{II}, Sn^{II} and Pb^{II} have a normal potential higher than that of the analyte, but with a difference that is smaller than 0.3 V. It is, therefore, improbable that they would be reduced first.

Ni^{II} and Co^{II} are capable of accelerating the hydrolysis reaction or decomposition of the reducing agent. An alkaline medium impedes the generation, and the comparison of potentials should, therefore, be carried out in this medium. As can be seen, this difference is favourable to the prior reduction of these elements in a basic medium (higher than 0.3 V). In this medium, a priority reduction to the elemental state can occur. As they have the same origin, both of these species should interfere in the same way; however, the experimental results show that Ni^{II} interferes much more severely than Co^{II}. The reason derives from the capacity of each, once precipitated to the elemental state, to retain the hydride and decompose it: Ni^{II} can do this more strongly than Co^{II}.

Sn^{II} and Pb^{II} are species that do not interfere, although they can be reduced preferentially to Sb^{III} independently of any previous hydrolysis of the reducing agent: they must, therefore, interfere by consuming the reducing agent or by adsorption on the precipitate. The explanation is to be found in the different kinetics of the processes being compared—the hydride formation process is faster than the formation of the elemental precipitate.

(3.2) Mo^{VI}, As^{III} and As^V, U^{VI}, Cu^{II}, Bi^{III}, Te^{VI}, Se^{IV} and Sn^{IV} all have the appropriate potential difference to be reduced preferentially to Sb^{III}, in both media: their interference is, therefore, justified. It might be interesting to investigate the possible mechanism further.

For the hydride-forming elements, and taking as a basis the previously cited work of Dittrich and Mandry,^{9,20} it is observed that: (i) As^{III}, As^V and Te^{VI} do not interfere: at the temperature of the flame, no formation of As–Sb or Te–Sb molecules occurs. Bi^{III} and Se^{IV} do interfere, partially by adsorption of the antimony hydride in solution by the elemental precipitate formed. (ii) The mechanism suggested to explain the interference of Sn^{IV} should be consistent with the non-interference of Sn^{II}, as the tin hydride can be generated from both oxidation states. For the Sn^{IV} species, the kinetics of the process of formation of the elemental precipitate is higher than that of hydride formation. The different behaviour produced in an HCl medium is explained by the formation of complex chlorates, which lower the reduction potential of Sn^{IV}.

Mo^{VI} and U^{VI} are species that are reduced to a lower oxidation state without reaching the elemental form. U^{VI} does not show any precipitate during the process and does not interfere. Mo^{VI} is reduced to one of its diverse oxidation states, precipitates a hydroxide or hydrated oxide, and does interfere.

An important aspect of Mo is that its interference is lower in an HNO₃ medium, which could indicate that its capacity to interfere may be related to the formation of some type of heteropolyacid with Sb, or with the appearance of some type of induced reaction given the complex redox properties of this element.

With Cu^{II}, only reduction to the elemental state occurs, producing adsorption of the antimony hydride in solution by the elemental precipitate formed.

CONCLUSIONS

The species studied here, and classified as non-interfering in previous papers, continue to be classified as non-interfering in each of the acid media studied.

From the results obtained, three conclusions can be drawn concerning the dependence both of the magnitude of the

interference and the mechanism that produces it on the generation medium.

(1) The interfering species Ni^{II}, Co^{II}, Cu^{II}, Bi^{III} and iodide ions are to be particularly noted owing to the observation of a distinct pattern in the variation of the signal. These species produce a progressive signal reduction with the concentration of added interferent and have a definite concentration range, different for each species, in which the signal is virtually independent of the concentration of the interferent. That is, it is observed that they have a similar action in qualitative terms but not quantitatively. If the sample contains any of the above elements, the best medium for the determination of Sb would be: HClO₄ for Cu^{II}, HClO₄ and HCl for Ni^{II}, and HCl and HNO₃ for Bi^{III}.

(2) When the sample to be analysed contains Al^{III}, the determination of Sb could be carried out in any of the acids studied except for HCl. If it contains Cr^{VI}, there is virtually no signal variation in HNO₃ when working with a concentration range below 600 µg.

(3) For Mo^{VI} and Sn^{IV}, the possibilities that the use of each medium offers should be studied for each particular sample.

With regard to mechanisms, the following are the most important conclusions.

(1) Neither the preferential consumption of reducing agent by the interferent, nor the possibility of reactions in the gas phase, is sufficient cause for interference, as had been supposed previously.

(2) The values of the normal reduction potentials for the different systems of the same element reflect what will be the behaviour of a species when it comes into contact with species of different elements in any acidic medium.

(3) The ability to predict the species that could produce a signal variation theoretically, using the potential values and before making the analysis. This applies not only to Sb but also to all those elements that can be determined by hydride formation.

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