

Study of the Interference of Iron and Mercury in the Determination of Antimony by Hydride Generation Atomic Absorption Spectrometry: Use of Speciation Models

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The use of computerised speciation models for studying the interference of iron in the determination of antimony by hydride generation atomic absorption spectrometry is discussed. The study is performed in four different acidic media, and a value of the Fe^{III} to Sb^{III} ratio is found above which the interference is observed to depend on the acidic medium. The effect of interference is explained by the oxidation of Sb^{III} to Sb^V and the generation of the hydride from the higher oxidation state. A new version of the computerised speciation model application Complex gives satisfactory explanations for these differences in terms of the modifications which the potential of the Fe^{III} - Fe^{II} system undergoes. This same methodology is used to explain the absence of interference from Hg^{II}.

Keywords: Antimony determination; hydride generation atomic absorption spectrometry; iron interference; mercury interference; computerised speciation model

Historically, the development of the analytical use of volatile covalent hydride generation has been directed fundamentally towards the study of reducing agents, acidic media,¹ generation systems and analytical techniques for detecting the hydride generated. The dual objectives were of obtaining better analytical response (sensitivity, detection limits and precision²) and performing multi-component determinations,^{3,4} as is the situation for hydride generation inductively coupled plasma atomic emission spectrometry (HG-ICP-AES) and hydride generation gas chromatography (HG-GC).

This search for improvements in analytical methodology has ignored, to a great extent, the systematic study of the processes of interference. Most published work has involved the development of analytical procedures to eliminate such interferences. Thus, for interferences on antimony hydride, interferent precipitation,⁵ the choice of a suitable acid concentration and generating system⁶ or the addition of KI or mixtures of KI with another reducer⁷ give the best results.

The combined hydride generation atomic absorption spectrometric (HG-AAS) method has, in general, fewer interferences than even methods involving electrothermal atomisation.⁸ However, most interference processes have not been studied fully, and the mechanisms are poorly controlled experimentally, so that most interpretations are subjective. The literature consulted in the course of the present study simply mentioned the appearance of interferences, and there are often differences between workers as to the effects observed. According to Hershey and Keliher⁶ such differences can be explained partly by the different interferent concentrations used, and partly by the different generation conditions.

Smith⁹ carried out the first complete study of interferences on Sb^{III} (in HG-AAS), examining the effect of 48 ions on the hydride signal, and proposed, as the main interference mechanism, the preferential reduction of the interfering ion to the elemental state, resulting in coprecipitation of the analyte or adsorption of the volatile covalent hydride formed, which could actually then be decomposed catalytically. This mechanism was also later endorsed by other workers.^{10,11}

Welz and Melcher¹² showed the correlation between the rate of precipitate formation during the reduction process and the interferent effect, while Meyer *et al.*¹³ suggested that the interferences do not always depend on the analyte to interferent ratio, nor on the prior contact time between the potential interferent ion and the analyte.

The results obtained by Yamamoto and Kumamaru¹⁴ were significant. They performed a comparative study between the use of Zn metal and sodium tetrahydroborate, and related the type of reducing agent to the degree of interference. Pierce and Brown^{8,15} investigated the dependence of the interference on the type of atomiser used. It would appear that silica tube atomisation is subject to fewer interferences, although a comparative study does not appear to have been carried out.

Dedina¹⁶ took an overview of all the interference mechanisms, and proposed a classification into groups of interferences arising in HG-AAS depending on whether they occur in the generation, transport or determination stage, and on whether the dominant mechanism is kinetic or not.

One of the most interesting elements from the point of view of interference is iron. In general, this element is present at relatively high concentrations in many types of samples which contain antimony at a trace level. Therefore the Fe^{III}:Sb^{III} ratio is very high. In spite of this, there is little agreement as to whether this element interferes¹⁴ or not,⁹ and to the extent and mechanism involved.

The present work involved an extensive study of the interference of Fe^{III} on the signal of antimony hydride, using four different acids. The apparent differences between the results obtained with the four acids and the mechanism of interference are explained by applying a mathematical model for speciation studies. The same methodology is used to study interference with Hg^{II}.

Experimental

Reagents

All reagents were of analytical-reagent grade (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 the sodium tetrahydroborate in doubly distilled water.

Table 1. Optimum conditions for antimony hydride generation

Acid	Concentration acid/M	Total volume/ml	NaBH ₄ concentration/% m/v	NaBH ₄ concentration/ml	Sb ³⁺ concentration/M
HCl	0.5	5.0	4	3.0	0.4928×10^{-5}
HNO ₃	0.5	5.0	4	3.0	0.4928×10^{-5}
H ₂ SO ₄	0.5	3.0	4	3.0	0.8214×10^{-5}
HClO ₄	0.5	3.0	3	3.0	0.8214×10^{-5}

Iron(III) solution, 2.5 M. Prepared by dissolving the appropriate amount of FeCl₃·6H₂O in doubly distilled water.

Mercury(II) solution, 1 M. Prepared by dissolving HgCl₂ in doubly distilled water.

In all instances working solutions were prepared by serial dilution of the stock solution with doubly distilled water immediately before use.

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.

Instrumental conditions used for the determination of antimony were: 217.6 nm wavelength; 0.2 nm bandwidth; acetylene flow-rate 2 l min⁻¹; and air flow-rate 24 l min⁻¹. Absorbance values were obtained in the continuous mode using the recorder but without background correction. The hydride generation and transport were carried out using a device described previously.¹

Procedure

To carry out the interference study, series of solutions containing the same amount of antimony (3 μg) and the acid concentrations being considered were prepared, but with varying amounts of added iron. The hydride generation conditions, which depend on the acid being used, have been studied previously¹ and are summarised in Table 1.

Results and Discussion

Study of the Interference of Iron

Fig. 1 shows the fall in the absorbance of antimony hydride as a function of iron concentration for each of the four acidic media in which generation was performed (Fe^{III}:Sb^{III} molar ratios below 50 had no effect on the signal). It can be seen that while the degree of interference depends on the amount of iron added and on the type of acid used in the generation, the graphs obtained are qualitatively similar, and consist of three distinct areas: firstly, where no interference is observed; secondly, where absorbance falls gradually with increasing iron concentration; and thirdly, where the absorbance is independent of iron concentration.

The mechanism proposed here to explain this interference is based on the fact that Fe^{III} can oxidise Sb^{III} to Sb^V. The antimony hydride is thus generated from the Sb in the higher valency state, and absorbance falls as the amount of SbH₃ generated from Sb^V decreases.¹⁷

Taking into account that the normal reduction potential of the Sb^V - Sb^{III} system is 0.75 mV, and that of the Fe^{III} - Fe^{II} system is 0.77 mV, this mechanism can qualitatively explain the graphs obtained: at low iron concentrations, the reduction potential of the Fe^{III} - Fe^{II} system is too low to oxidise Sb^{III}, so that no interference is observed. As the iron concentration increases, so does the reduction potential of the Fe^{III} - Fe^{II} system, until the amount of Sb^{III} has been oxidised to such a degree that the signal then begins to fall. The signal falls

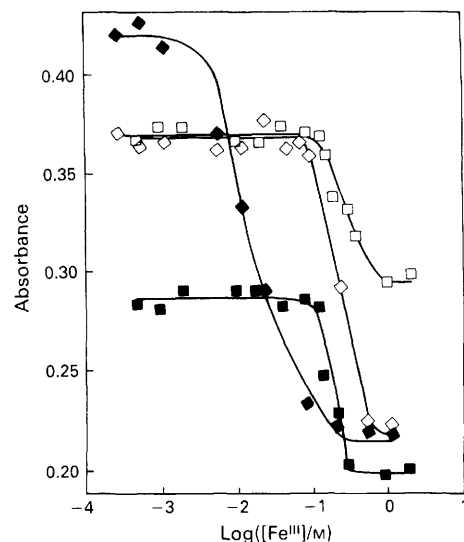


Fig. 1. Change in SbH₃ absorbance with increasing amounts of Fe^{III} added to the four acid media. ◆, HCl; ◇, HNO₃; □, H₂SO₄; and ■, HClO₄.

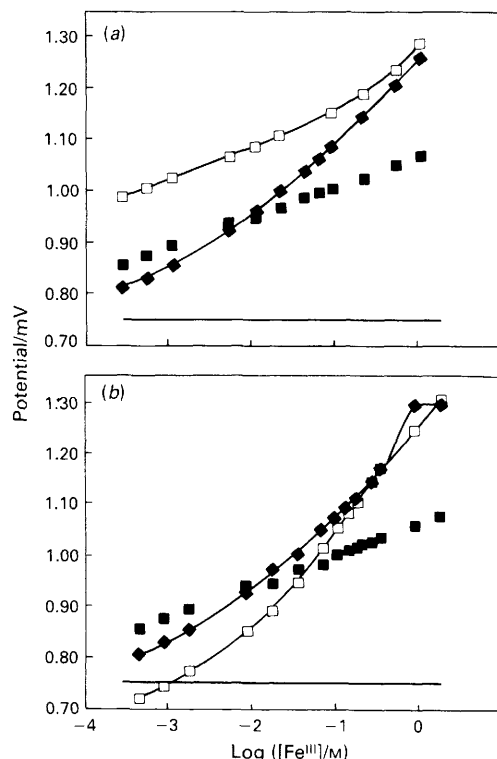


Fig. 2. (a) Effect of increasing Fe^{III} concentration on the solution potential. □, HCl; ◆, HNO₃; ■, Fe^{III} - Fe^{II} potential if complex formation is not considered; and —, Sb^V - Sb^{III} potential. (b) Effect of increasing Fe^{III} concentration on the solution potential. □, H₂SO₄; ◆, HClO₄; ■, Fe^{III} - Fe^{II} potential if complex formation is not considered; and —, Sb^V - Sb^{III} potential. The horizontal lines without data points represent the theoretical potential.

Table 2. Results obtained from the computer speciation model applied to the Fe^{III} interference study. The species in bold are the most predominant

Fe ^{III} added/ mol l ⁻¹	HCl		HNO ₃	
	Predominant chemical species	Fe ^{III} free/ mol l ⁻¹	Predominant chemical species	Fe ^{III} free/ mol l ⁻¹
0.2703 × 10 ⁻³	FeCl₂⁺, FeCl₂²⁺	0.5420 × 10 ⁻⁵	Fe(NO₃)₂²⁺, Fe³⁺	0.4406 × 10 ⁻⁴
0.5407 × 10 ⁻³	FeCl₂⁺, FeCl₂²⁺	0.1093 × 10 ⁻⁴	Fe(NO₃)₂²⁺, Fe³⁺	0.8860 × 10 ⁻⁴
0.1081 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺	0.2190 × 10 ⁻⁴	Fe(NO₃)₂²⁺, Fe³⁺	0.1766 × 10 ⁻³
0.5407 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺	0.1078 × 10 ⁻³	Fe(NO₃)₂²⁺, Fe³⁺, FeCl₂⁺	0.8326 × 10 ⁻³
0.01081	FeCl₂⁺, FeCl₂²⁺	0.2108 × 10 ⁻³	Fe(NO₃)₂²⁺, Fe³⁺, FeCl₂⁺	0.1542 × 10 ⁻²
0.02163	FeCl₂⁺, FeCl₂²⁺	0.4028 × 10 ⁻³	Fe(NO₃)₂²⁺, FeCl₂⁺, Fe³⁺	0.2664 × 10 ⁻²
0.04325	—	—	Fe(NO₃)₂²⁺, FeCl₂⁺, FeCl₂⁺	0.4120 × 10 ⁻²
0.06488	—	—	Fe(NO₃)₂²⁺, FeCl₂⁺, FeCl₂⁺	0.4984 × 10 ⁻²
0.08651	FeCl₂⁺, FeCl₂²⁺	0.1260 × 10 ⁻²	FeCl₂⁺, Fe(NO₃)₂²⁺, FeCl₂⁺	0.5526 × 10 ⁻²
0.2163	FeCl₂⁺, FeCl₂²⁺	0.2128 × 10 ⁻²	FeCl₂⁺, FeCl₂⁺, Fe(NO₃)₂²⁺	0.6409 × 10 ⁻²
0.5407	FeCl₂⁺, FeCl₂²⁺	0.2677 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺	0.5618 × 10 ⁻²
1.081	FeCl₂⁺, FeCl₂²⁺	0.2553 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺	0.4253 × 10 ⁻²
H ₂ SO ₄		HClO ₄		
Fe ^{III} added/ mol l ⁻¹	Predominant chemical species	Fe ^{III} free/ mol l ⁻¹	Predominant chemical species	Fe ^{III} free/ mol l ⁻¹
0.4506 × 10 ⁻³	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.2101 × 10 ⁻⁵	FeClO₄²⁺, Fe³⁺	0.4936 × 10 ⁻⁴
0.9011 × 10 ⁻³	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.4249 × 10 ⁻⁵	FeClO₄²⁺, Fe³⁺	0.9923 × 10 ⁻⁴
0.1802 × 10 ⁻³	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.8575 × 10 ⁻⁵	FeClO₄²⁺, Fe³⁺	0.1977 × 10 ⁻³
0.9011 × 10 ⁻²	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.4454 × 10 ⁻⁴	FeClO₄²⁺, Fe³⁺, FeCl₂⁺	0.9261 × 10 ⁻³
0.01802	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.9282 × 10 ⁻⁴	FeClO₄²⁺, FeCl₂⁺, Fe³⁺	0.1695 × 10 ⁻²
0.03604	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.1998 × 10 ⁻³	FeClO₄²⁺, FeCl₂⁺, FeCl₂⁺	0.2852 × 10 ⁻²
0.07209	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻	0.4460 × 10 ⁻³	FeClO₄²⁺, FeCl₂⁺, FeCl₃⁺	0.4215 × 10 ⁻²
0.1081	Fe(SO₄)₂²⁺, Fe(SO₄)₂⁻, FeCl₂⁺	0.7107 × 10 ⁻³	FeClO₄²⁺, FeCl₂⁺, FeCl₂⁺	0.4931 × 10 ⁻²
0.1442	Fe(SO₄)₂²⁺, FeCl₂⁺, Fe(SO₄)₂⁻	0.9669 × 10 ⁻³	FeCl₂⁺, FeCl₂⁺, FeClO₄²⁺	0.5329 × 10 ⁻²
0.1802	Fe(SO₄)₂²⁺, FeCl₂⁺, FeCl₂²⁺	0.1199 × 10 ⁻²	FeCl₂⁺, FeCl₂⁺, FeClO₄²⁺	0.5549 × 10 ⁻²
0.2163	—	—	FeCl₂⁺, FeCl₂⁺, FeClO₄²⁺	0.5663 × 10 ⁻²
0.2703	Fe(SO₄)₂²⁺, FeCl₂⁺, FeCl₂²⁺	0.1652 × 10 ⁻²	FeCl₂⁺, FeCl₂⁺, FeClO₄²⁺	0.5715 × 10 ⁻²
0.3604	Fe(SO₄)₂²⁺, FeCl₂⁺, FeCl₂²⁺	0.1953 × 10 ⁻²	FeCl₂⁺, FeCl₂⁺, FeClO₄²⁺	0.5636 × 10 ⁻²
0.9011	FeCl₂⁺, Fe(SO₄)₂²⁺, FeCl₂²⁺	0.2443 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺	0.4453 × 10 ⁻²
0.1802	FeCl₂⁺, Fe(SO₄)₂²⁺, FeCl₂²⁺	0.2206 × 10 ⁻²	FeCl₂⁺, FeCl₂²⁺, FeCl₃	0.3135 × 10 ⁻²

sequentially as the interferent concentration increases, until all the analyte is oxidised. Therefore, higher Fe^{III} concentrations will have no further effect on the signal.

However, this model does not explain why the interferences occur at different Fe^{III} concentrations, nor the subsequent progression of the interference curves, when different acids are used in the generation of the hydride.

To investigate this aspect further, a theoretical study was performed to find the predominant physico-chemical species, both of Fe^{III} and of Sb^{III}, present in each test. This should enable the determination of the concentrations of free Fe^{III} and Sb^{III}, hence the actual redox potential of the solution and therefore the degree of interference. This speciation study was performed using a new version, developed in this department, of the program Complex. This program uses an algorithm based on the brute force convergence method.¹⁸ In each instance the following values were introduced into the program: the concentrations of each species added, the acidity of the solutions and the values of the equilibrium constants (including hydrolysis constants) of the different complexes which might be formed.¹⁹

It should be taken into account that the Fe^{III} is added to the solution as iron(III) chloride (FeCl₃). Therefore, when the amount of Fe is low, the amount of Cl⁻ is correspondingly low, and the program shows that the cation is present in compounds with the anion of the acid added for generation (Table 2). As the amount of iron added to the generator increases, so does the amount of Cl⁻. Therefore, with the exception of sulphuric acid, where the predominant species is still the sulphate complex of Fe^{III}, the predominant species in the other three acids are chloro-complexes of iron.

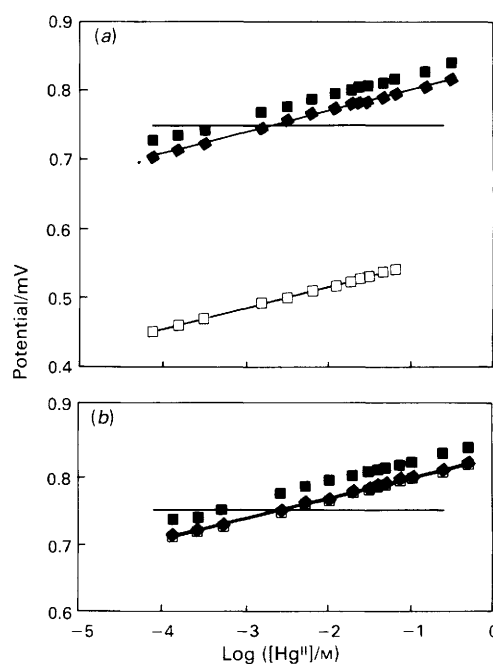


Fig. 3. (a) Effect of increasing Hg^{II} concentration on the solution potential. □, HCl; ◇, HNO₃; ■, Hg^{II} - Hg potential if complex formation is not considered; and —, Sb^V - Sb^{III} potential. (b) Effect of increasing Fe^{III} concentration on the solution potential. □, H₂SO₄; ◆, HClO₄; ■, Hg^{II} - Hg potential if complex formation is not considered; and —, Sb^V - Sb^{III} potential. The horizontal lines without data points represent the theoretical potential

Table 3. Results obtained from the computer speciation model applied to the Hg^{II} interference study. The species in bold are the most predominant

Hg ^{II} added/ mol l ⁻¹	HCl		HNO ₃	
	Predominant chemical species	Hg ^{II} free/ mol l ⁻¹	Predominant chemical species	Hg ^{II} free/ mol l ⁻¹
0.7478 × 10 ⁻⁴	HgCl₄²⁻ , HgCl ₃ ⁻	0.7598 × 10 ⁻¹⁸	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.1665 × 10 ⁻⁴
0.1496 × 10 ⁻³	HgCl₄²⁻ , HgCl ₃ ⁻	0.1521 × 10 ⁻¹⁷	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.3081 × 10 ⁻⁴
0.2991 × 10 ⁻³	HgCl₄²⁻ , HgCl ₃ ⁻	0.3047 × 10 ⁻¹⁶	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.6150 × 10 ⁻⁴
0.1496 × 10 ⁻²	HgCl₄²⁻ , HgCl ₃ ⁻	0.1548 × 10 ⁻¹⁶	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.3072 × 10 ⁻³
0.2991 × 10 ⁻²	HgCl₄²⁻ , HgCl ₃ ⁻	0.3157 × 10 ⁻¹⁶	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.6144 × 10 ⁻³
0.5982 × 10 ⁻²	HgCl₄²⁻ , HgCl ₃ ⁻	0.6570 × 10 ⁻¹⁶	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.1229 × 10 ⁻²
0.01196	HgCl₄²⁻ , HgCl ₃ ⁻	0.1425 × 10 ⁻¹⁵	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.2457 × 10 ⁻²
0.01795	HgCl₄²⁻ , HgCl ₃ ⁻	0.2318 × 10 ⁻¹⁵	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.3687 × 10 ⁻²
0.02393	HgCl₄²⁻ , HgCl ₃ ⁻	0.3356 × 10 ⁻¹⁵	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.4915 × 10 ⁻²
0.02991	HgCl₄²⁻ , HgCl ₃ ⁻	0.4563 × 10 ⁻¹⁵	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.6144 × 10 ⁻²
0.04487	HgCl₄²⁻ , HgCl ₃ ⁻	0.8472 × 10 ⁻¹⁵	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.9216 × 10 ⁻²
0.05982	HgCl₄²⁻ , HgCl ₃ ⁻	0.1405 × 10 ⁻¹⁴	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.01229
0.1496	—	—	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.03072
0.2991	—	—	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.06144

Hg ^{II} added/ mol l ⁻¹	Predominant chemical species	Hg ^{II} free/mol l ⁻¹	
		H ₂ SO ₄	HClO ₄
0.1246 × 10 ⁻³	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.2153 × 10 ⁻⁴	0.2774 × 10 ⁻⁴
0.2493 × 10 ⁻³	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.4293 × 10 ⁻⁴	0.5134 × 10 ⁻⁴
0.4985 × 10 ⁻³	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.8574 × 10 ⁻⁴	0.1025 × 10 ⁻³
0.2493 × 10 ⁻²	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.4282 × 10 ⁻³	0.5120 × 10 ⁻³
0.4985 × 10 ⁻²	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.8564 × 10 ⁻³	0.1024 × 10 ⁻²
0.9971 × 10 ⁻²	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.1713 × 10 ⁻²	0.2048 × 10 ⁻²
0.01994	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.3427 × 10 ⁻²	0.4096 × 10 ⁻²
0.02991	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.5143 × 10 ⁻²	0.6143 × 10 ⁻²
0.03988	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.6859 × 10 ⁻²	0.8191 × 10 ⁻²
0.04985	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.8577 × 10 ⁻²	0.01024
0.07478	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.01288	0.01536
0.09971	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.01718	0.02048
0.2493	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.04317	0.05119
0.4985	HgCl₂ , HgCl ⁺ , Hg ²⁺	0.8700	0.1024

For antimony, there are differences depending on the acidic medium and on the amount of iron (and hence, chloride) present. Thus, if generation is performed in HCl, the chloro-complexes of Sb^{III} are the predominant species, at any concentration of Fe^{III}. At low interferent concentrations, when generation is performed in any of the other three acidic media, and given that Sb^{III} does not form stable complexes with any of these three anions, the predominant species is that produced by hydrolysis. As the concentration of iron increases, so does that of chloride, so that again chloro-complexes of antimony will predominate. As Sb^{III} is present at lower concentrations than free Fe^{III} at all times, the final potential of the system will not be affected by these variations in the concentration of free Sb^{III}.

Therefore, the presence of these complexes makes the concentration of free Fe^{III} in solution much lower than the actual amount added, so that the actual potential of the Fe^{III} - Fe^{II} system is not the value expected on the basis of the Nernst equation. Fig. 2 shows the estimated value of this potential as a function of the amount of added iron, for each of the acids, together with the value that potential would have if the complexing equilibria were not considered. According to this graph, when hydride generation is performed from HCl, the iron will begin to interfere at lower concentrations than in the other acids and, furthermore, as the potential of the Fe^{III} - Fe^{II} system increases faster in this medium than in the other three, the interference should be more pronounced. When perchloric or nitric acid is used, the potential of the Fe^{III} - Fe^{II} system increases in the same way as in HCl, but more slowly, so that the interference should appear at higher concentrations of Fe^{III}, and be less incisive. In sulphuric acid, the potential of the interferent system develops faster than in nitric or perchloric acids, but as the initial potential is lower,

the interference initially appears at concentrations of iron which are slightly higher than for the other acids. These conclusions agree with the experimental results shown in Fig. 1. As anticipated, although the interference appears at different Fe^{III}:Sb^{III} ratios, the potential of the Fe^{III} - Fe^{II} system is always the same (in the order of 1.05 mV), 0.3 mV higher than that of the Sb^V - Sb^{III} system.

Study of the Interference of Mercury

The mathematical speciation model explains the results obtained with iron. The same model can also be used to explain the fact that potential interferents, such as Hg^{II}, do not interfere.

Mercury does not interfere in any way with the antimony hydride signal in any of the four acids. However, the normal reduction potential of the Hg^{II} - Hg system (0.80 mV) is sufficient to oxidise Sb^{III} to Sb^V, so that we would expect a fall in the hydride signal at even lower concentrations than with Fe^{III}.

The interferent solution was prepared, as described earlier, from mercury(II) chloride. This cation forms very stable chloro-complexes, and much less stable nitrate and sulphate complexes, while it forms no known complex with perchlorate ions. Table 3 shows how, after running the program, the predominant species in all instances is found to be a chloro-complex, and that the concentration of free cation is very low. From this concentration, a value of the reduction potential of the Hg^{II} - Hg system, shown in Fig. 3, was found for each situation.

Clearly, although the normal potential of the Hg^{II} - Hg system is higher than that of Fe^{III} - Fe^{II}, the amount of free Hg^{II} is so small that the potential only slightly increases the

effect of concentration, and in no instance does it reach 1.05 mV, the value established as the critical interference value for iron. Therefore, no interference is observed with this cation in any of the four acids studied.

Conclusions

Studying the physico-chemical species in which an analyte or potential interferent is present in solution can, in some instances, clarify the processes by which a chemical species does or does not interfere in hydride generation. This suggests possible areas for further study. One important conclusion of the present work is that the type of compound or standard must be considered very carefully.

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References

1. Sanz, J., Martinez, M. T., Galban, J., and Castillo, J. R., *At. Spectrosc.*, 1988, **9**, 63.
2. Castillo, J. R., Mir, J. M., and Martinez, M. C., *Quim. Anal.*, 1986, **6**, 33.
3. Thompson, M., Pahlavanpour, B., Walton, S. J., and Kirkbright, G. F., *Analyst*, 1978, **103**, 568.
4. Fleming, H. D., and Ide, R. G., *Anal. Chim. Acta*, 1976, **86**, 67.
5. Thompson, M., Pahlavanpour, B., Walton, S. J., and Kirkbright, G. F., *Analyst*, 1978, **103**, 705.
6. Hershey, J. W., and Keliher, P. N., *Spectrochim. Acta, Part B*, 1986, **41**, 713.
7. Yamamoto, M., Sholji, T., Kumamaru, T., and Yamamoto, Y., *Fresenius Z. Anal. Chem.*, 1981, **305**, 11.
8. Pierce, F. D., and Brown, H. R., *Anal. Chem.*, 1977, **49**, 1417.
9. Smith, A. E., *Analyst*, 1975, **100**, 300.
10. Verlinde, M., and Deelstra, H., *Fresenius Z. Anal. Chem.*, 1979, **296**, 253.
11. Kirkbright, G. F., and Toddia, M., *Anal. Chim. Acta*, 1978, **100**, 145.
12. Welz, B., and Melcher, M., *Spectrochim. Acta, Part B*, 1981, **36**, 439.
13. Meyer, A., Hofer, Ch., Tolg, E., Raptis, S., and Knapp, G., *Fresenius Z. Anal. Chem.*, 1979, **296**, 337.
14. Yamamoto, Y., and Kumamaru, T., *Fresenius Z. Anal. Chem.*, 1976, **281**, 353.
15. Pierce, F. D., and Brown, H. R., *Anal. Chem.*, 1976, **48**, 693.
16. Dedina, J., *Anal. Chem.*, 1982, **54**, 2097.
17. Welz, B., Melcher, M., and Sinemus, H. W., *At. Spectrosc.*, 1981, **2**, 81.
18. Ginzburg, G., *Analyst*, 1976, **23**, 149.
19. Smith, R. M., and Martell, A. E., "Critical Stability Constants. Volume 4: Inorganic Complexes," Plenum Press, New York, 1976.

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