

# Mutual Interferences of Hydride-Forming Elements in Gaseous Phase

<sup>a</sup>E. KRAKOVSKÁ and <sup>b</sup>D. MACKOVÝCH

<sup>a</sup>Department of Chemistry, Faculty of Metallurgy,  
Technical University, SK-042 00 Košice

<sup>b</sup>Slovak Geology, Geological and Ecological Laboratories,  
SK-052 40 Spišská Nová Ves

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The mutual interferences were studied on the model solutions and the value of maximum concentration of the interferent element in solution was determined. This is defined as such a concentration value, by which no interferences are yet caused. The results from interference studies presented in this work provide practical information on mutual interaction effect value of As, Bi, Sb, Se, and Te.

The so-called hydride technique is applied in the AAS method for low concentration determination of analytes that form gaseous hydrides with atomic hydrogen. These analytes are released from the solution during the chemical reaction with a reducing agent such as SnCl<sub>2</sub> or ZnCl<sub>2</sub> in the presence of HCl in the form of gaseous hydrides which are atomized at relatively low temperature. The hydride of the analyte determined is introduced into some tube, for instance silica tube placed in the optical axis of the spectrometer and heated by the atomizer flame. Here it dissociates forming free atoms of analyte which are the source of the analytical signal. Recently, NaBH<sub>4</sub> is used as agent for efficient hydride formation process [1]. It may be applied for formation of As, Bi, Ge, Sb, Se, Sn, Te [2], and Pb [3] hydrides. The generation of hydrogen and reduction of analyte proceeds then according to the scheme [4]



E is analyte,  $m^+ = n$  or  $m^+ \neq n$

The method of hydride generation ensures chemical separation of the analyte from the interferents in solution and, at the same time, ensures preconcentration of the elements determined lowering thus the detection limit. In comparison with the classical flame AAS technique, the detection limit may be better of approximately two orders of magnitude.

Interferences arising during the application of the hydride technique in AAS originate in both liquid and

gaseous phase. *Dědina* [5] classified interferences in liquid as well as gaseous phase according to the place and reason of their origin.

Remarkable influence on the hydride formation efficiency is exhibited by the types of analytes in the solution, e.g. significant role is played by the oxidation state of the analyte, concentration of the reducing agent, concentration and kind of the acid, and presence of the interfering substances. Many authors studied these and other factors influencing the hydride formation efficiency. Generalization of the knowledge achieved is however not wholly justified since the hydride techniques studied were not identical.

It was proved that the hydride generation from lower oxide states of analytes is more efficient. This fact is commonly known and accepted and logically follows from the reaction mechanisms.

Several authors dealt with the optimization of kind and concentration of the reducing agent. When using NaBH<sub>4</sub> as reducing agent, which is at present used most frequently, a higher efficiency can be reached by application of its solution in continual methods of hydride generation [6–8]. Optimum results were reached in case of hydride generation from HCl solutions of various concentrations [9–18].

## EXPERIMENTAL

Mutual interferences of the hydride-forming elements were studied on model solutions of As, Bi, Sb, Se, Te, Pb, and Sn. The solutions of the concentration  $\rho = 1 \text{ mg cm}^{-3}$  were prepared from substances of spectral purity supplied by the Slovak Metrological Institute in Bratislava. Stock solutions of analytes

Table 1. Influence of the Interferents Concentration upon the Signal of Selenium

Interferent	Depression of the signal of Se/%					
	0		10		50	
	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$
	$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$	
As(III)	0.40	20	0.80	40	2.00	100
As(V)	0.40	20	1.20	60	5.00	250
Sb(III)	0.20	10	0.50	25	1.50	75
Sb(V)	5.00	250	15.00	750	30.00 <sup>a</sup>	1500
Bi(III)	0.30	15	0.76	375	5.0	250
Te(IV)	5.00	250	20.00	1000	30.00 <sup>a</sup>	1500

a) 20 % depression of the signal of Se.

Table 2. Influence of the Interferents Concentration upon the Signal of Arsenic

Interferent	Depression of the signal of As/%					
	0		10		50	
	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$
	$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$	
Sb(III)	0.02	1	0.10	5	0.50	25
Bi(III)	1.0	50	40.00	2000	—	—
Te(IV)	0.10	5	0.50	25	5.00	250

and interferents were diluted stepwise. Concentration of  $\text{NaBH}_4$  was optimized in advance. Sodium tetrahydridoborate was supplied by Loba Feinchemie, Austria and argon of 99.999 % purity by Linde. Technical acetylene (Chemko Strážske) was purified before entering the measuring equipment with concentrated  $\text{H}_2\text{SO}_4$ .

A Varian spectrometer AA 400 was used for absorbance of As, Bi, Sb, Se, and Te measurements. Lamp current used for all analytes was 10 mA. Continual hydride generator VGA 76 (Varian) with silica tube and three canals was used for hydride generation. Flow rate of the sample was  $7 \text{ cm}^3 \text{ min}^{-1}$ , flow rates of the acid and of  $\text{NaBH}_4$   $1 \text{ cm}^3 \text{ min}^{-1}$ . Concentration of HCl was  $3 \text{ mol dm}^{-3}$  and mass fraction of  $\text{NaBH}_4$  0.6 %. Further working conditions for various analytes are as follows

Element	As	Bi	Sb	Se	Te
Wavelength/nm	193.7	223.1	217.6	196.0	214.3
Slit width/nm	0.2	0.2	0.2	1.0	0.2

Hydrides of the studied elements were generated from 3 M-HCl solution. The value of the acid concentration was optimized with regard to its influence upon the absorbance signal of the respective analytes. The influence of HCl was investigated in 1 to 6 M solutions.

## RESULTS AND DISCUSSION

It was observed that the absorbance signal value of the studied hydrides varied only slightly in the concentration interval used. Thus, any concentration from this interval may be chosen and is suitable for practical application.

In order to compare the extent of the interference element influence upon the investigated analyte, the following parameters were determined: the maximum interference element concentration in the analyzed solution not yet causing a decrease in the analyte signal; the value of  $c(I)/c(A)$  determining the limiting interference element to analyte concentrations ratio not yet causing a decrease in the analyte signal; the "limit of toleration" value; and the "critical concentration" value.

The expression "limit of toleration" [5] is a concentration of interferent able to decrease the signal of analyte by 10 %. The "critical concentration" causes a 50 % decrease in the signal of analyte.

The expression  $c(I)/c(A)$  represents the interferent to analyte concentration ratio. In practical analysis, this ratio enables to identify the excess of interferent not yet causing the depression of the analyte signal and thus an incorrect result. Data given in Tables 1—5 represent results with 0 % error. If a 10 % decrease in the analyte signal is caused by the interferent the

**Table 3.** Influence of the Interferents Concentration upon the Signal of Bismuth

Interferent	Depression of the signal of Bi/%					
	0		10		50	
	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$
	$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$	
Se(IV)	0.05	2.5	0.10	5	0.50	25
Te(IV)	0.20	10	0.30	15	1.00 <sup>a</sup>	50
Sb(III)	1.00	50	7.00	350	20.00 <sup>b</sup>	1000
Sb(V)	10.00	500	25.00	1250	50.00 <sup>b</sup>	2500

a) 20 % depression of the signal of Bi; b) 25 % depression of the signal of Bi.

**Table 4.** Influence of the Interferents Concentration upon the Signal of Antimony

Interferent	Depression of the signal of Sb/%					
	0		10		50	
	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$
	$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$	
As(III)	0.20	10	0.50	25	4.00	200
Bi(III)	0.50	25	2.00	100	15.00 <sup>a</sup>	750
Te(IV)	0.20	10	0.50	25	10.00	500

a) 20 % depression of the signal of Sb.

**Table 5.** Influence of the Interferents Concentration upon the Signal of Tellurium

Interferent	Depression of the signal of Te/%					
	0		10		50	
	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$	$\rho(I)$	$\rho(I)/\rho(A)$
	$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$		$\mu\text{g cm}^{-3}$	
As(III)	0.05	2.5	0.2	10	2.0	100
As(V)	0.1	5	1.0	50	10.0	500
Sb(III)	0.05	2.5	0.5	25	2.0	100
Sb(V)	2.0	100	10.0	500	20.0 <sup>a</sup>	1000
Bi(III)	3.0	150	4.0	200	35.0	1750
Se(IV)	0.1	5	0.2	10	0.7	35

a) 20 % depression of the signal of Te.

analytical result is burdened by systematic negative yet acceptable error. A decrease of 50 % makes the analytical result unacceptable. The determined values of  $c(I)/c(A)$  are valid for concentration ratios and working conditions given in the present work or not significantly different ones.

Influence of interferents concentration upon the signals of Se, As, Bi, Sb, and Te is expressed as limit of toleration, critical concentration, and the non-reduced absorbance signal of analyte expressed as the  $c(I)/c(A)$  ratio. Tables 1—5 present all three above pa-

rameters whereas Table 6 summarizes only the non-reduced signals for all studied analytes.

The results of the study of mutual interferences of the hydride-forming elements summarized in Table 6 give the values of the  $c(I)/c(A)$  ratio which is the interferent to analyte concentrations ratio not yet causing a decrease in the signal of analyte. From this it follows that the most significant influence upon the analytes of hydride-forming elements is exhibited by Sb(III). Less significant is its influence during the atomization of Bi(III), most likely due to different mechanisms of

**Table 6.** Values of the  $\rho(I)/\rho(A)$  Ratio at the Nonreduced Absorbance Signal of Analyte

Interferent	Analyte				
	As(III)	Bi(III)	Sb(III)	Se(IV)	Te(IV)
As(III)	–	N	10	20	2.5
As(V)	–	N	–	20	5
Bi(III)	50	–	25	15	150
Sb(III)	1	50	–	10	2.5
Sb(V)	–	500	–	250	100
Se(IV)	N	2.5	N	–	5
Te(IV)	5	10	10	250	–
Sn(II)	500	2500	2500	1000	–
Pb(II)	2500	2500	2500	2500	–

Concentration of analytes  $\rho(A) = 20 \text{ ng cm}^{-3}$ ; N – nonreducing effect in these conditions; Sb(V) and As(III) or As(V) and Sb(III) cannot exist together. Both of them have identical oxidation state.

both hydrides generation.

Further significant interferents are As(III) and Se(IV). This is an evidence for the fact that hydride-forming analytes in a lower oxidation state exhibit a more significant interfering effect owing to a more efficient hydride formation from these compounds.

Comparing the results of the interference study with literature data, some differences arise which may be attributed both to the application of various types of hydride generators and the differences in the reaction conditions. The aim of this study was to determine the numerical values of the interferent to analyte concentration ratio not yet exhibiting any influence upon the signal of analyte, in order to apply it in practical work. The study is concerned with binary interferences of the hydride-forming elements but the summarizing effect of them may be assumed, too. This summarizing effect is important in the case of interferences of hydride-forming elements in lower oxidation state (As(III), Sb(III), Se(IV)). Here, remarkable competitive reduction reactions proceed and casual shortage of atomic hydrogen needed for the reduction of analyte occurs. The influence of the interferents concentration upon the signal of analyte for the system presented may be estimated with 10 % accuracy on the basis of linear addition of the effects. Application of higher reduction agent concentration specified as optimum for the given hydride system does not lead to the solution of the problem. After mixing the reduction agent, acid, and analyte solution huge amount of gaseous hydrogen would be released which would negatively affect the analytical determination.

## REFERENCES

1. Smidt, F. J. and Royer, J. L., *Anal. Lett.* 6, 17 (1971).
2. Fernandez, F. J., *At. Absorpt. Newslett.* 12, 6 (1973).
3. Thompson, K. C. and Thomerson, D. R., *Analyst* (London) 99, 595 (1974).
4. Dalton, E. F. and Malonski, A. J., *At. Absorpt. Newslett.* 10, 92 (1971).
5. Dědina, J., *Anal. Chem.* 54, 2097 (1982).
6. Narsito and Agterdenbos, J., *Anal. Chim. Acta* 11, 315 (1987).
7. Buttler, M. J. and Smidt, D. C., *J. Anal. At. Spectrosc.* 3, 731 (1990).
8. Narsito, Agterdenbos, J., and Santosa, S. J., *Anal. Chim. Acta* 237, 189 (1990).
9. Hobbins, W. B., *Varian Techtron Instrument at Work* AA 11 (1981).
10. Narasaki, H. and Ikeda, M., *Anal. Chem.* 56, 2059 (1984).
11. Chan, C. C. Y. and Sadana, R. S., *Anal. Chim. Acta* 270, 231 (1992).
12. Hobbins, W. B., *Varian Techtron Instrument at Work* AA 22 (1982).
13. Oliviera de, E., McLaren, J. W., and Berman, S. S., *Anal. Chem.* 55, 2047 (1983).
14. Nakahara, T. and Sunahara, T., *Anal. Chim. Acta* 172, 127 (1985).
15. Hahn, M. H., Wolnik, K. A., and Fricke, F. L., *Anal. Chem.* 54, 1048 (1982).
16. Tsalev, D. L. and Manduykov, P. B., *J. Anal. At. Spectrosc.* 2, 135 (1987).
17. Krakovská, E. and Mackových, D., *Proceedings of the XIIth Seminar on Atomic Spectroscopy*, p. 63. Štrbské Pleso, 1994.
18. Krakovská, E. and Mackových, D., *Abstr. XXIXth Coll. Spectr. Int.*, p. 291. Leipzig, 1995.

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