

Possibility to eliminate interferences of mineral acids in optical emission spectroscopy with inductively coupled plasma

J. KUBOVÁ and V. STREŠKO

*Geological Institute, Faculty of Natural Sciences,
Comenius University, CS-842 15 Bratislava*

Received 4 June 1990

In the present paper the influence of HCl, HNO₃, H₃PO₄, and H₂SO₄ on the determination of Cd, Cr, Cu, Pb, and Zn has been evaluated. At higher acid concentrations a partial elimination of their depressive influence on the intensity of spectral lines can be achieved by an appropriate choice of the observation height, different from its commonly used value (optimized for the maximum signal to background ratio).

It is true that the detection limit is worsened by the procedure, but at the claim for accurate determinations of contents exceeding considerably the limit of detection it does not play primary role. Experimentally obtained results were checked by the analysis of attested reference geological materials.

The described method enabling a lowering of the interference of acid matrix is not pretentious concerning the duration of the analysis and it does not require any additional sample treatment.

Optical emission spectroscopy with inductively coupled plasma (OES-ICP) belongs at present to mostly used multielement procedures for the analysis of aqueous solutions. In spite of the fact that the first papers [1—3] devoted to analytical applications of the method referred the absence of interferences, in later ones [4—8], manifold and complex interelement interferences were stated. Even the presence of common mineral acids showed an influence on the intensity of analytical signals and so on the reliability of the gained analytical results. It was found that the presence of mineral acids caused generally a depression of analytical signals corresponding to the analyzed elements [9—12].

Maessen [9] studied the influence of different HCl, H₂SO₄, HNO₃ concentrations on the intensity of spectral lines for some elements, using various kinds of nebulization of sample and controlled uptake rate. Changes in the magnitude of the influence caused by acids cannot be explained only by changes in viscosity of solution, but they are closely connected also with excitation conditions in the plasma. Small differences in the used plasma power, as well as changes of the observation height show a considerable influence on the interference of acids [13, 11]. An opposite influence of acids, *i.e.* an enhancement of the signal is

connected with "adaptation" properties of acids. It means that a time has to be allowed for to ensure stable conditions of the system: nebulizer, spray chamber and injector; this time varies for samples containing different concentration and different kind of acid. So, *e.g.* for samples with a content of 0.05—20 % HCl the "adaptation time" corresponds to *ca.* 3—5 min [9].

Several methods were proposed for performing a correction of the influence of mineral acids on the analytical results obtained using aqueous solutions. The majority of them claims, however, long-lasting procedures.

A simple and commonly used procedure consists in the simulation of the composition of the sample solutions by the composition of reference calibration solutions [14, 15].

Methods based on the use of internal reference elements can improve the short-time precision, the instrumental drift, as well as the compensation of the matrix influence [16—19]. Unfortunately, the use of this technique is restricted by the fact that the precision and accuracy are influenced by different action of the basic composition of samples, therefore a simple criterion for the choice of internal reference elements and their appropriate spectral lines cannot be easily defined. It means that apart from instrumental restrictions and long duration of analyses, the choice of one or more internal reference elements for 50 or more analytical spectral lines represents a complex problem [20].

The standard addition technique can also be applied for correction of matrix interferences, but it is time-consuming. Its promising variation designed as "generalized standard addition method" needs extended data and calculations [21].

All listed methods make, however, the sample preparation longer and/or complicated. There are therefore efforts to work out procedures for the correction of matrix, inclusive acid interferences which would enable the analysis of any type of samples by the use of only one set of calibration solutions ensuring accurate results. *Botto* [22] proposed a method for correction of matrix, or acid and salt interferences in OES-ICP based on the measurement of a hydrogen spectral line as reference. The procedure needs neither a use of specially added internal reference elements, nor exact matrix simulation or standard additions.

In the present work we endeavoured a quantitative evaluation of the influence of the mineral acids HCl, HNO₃, H₂SO₄, and H₃PO₄ on the determination of some elements and to suppress or correct these interferences by the change of the observation height as indicated in [23, 24].

Experimental

The following instruments were used for the measurements:

Spectrometer Plasmakon S 35 (Kontron, FRG), sequential, with grating 2400

lines mm^{-1} ; Ar/Ar plasma: power 1.25 kW, flow rate of cooling gas $14.6 \text{ dm}^3 \text{ min}^{-1}$, of plasma gas $0.5 \text{ dm}^3 \text{ min}^{-1}$, of carrier gas $1.5 \text{ dm}^3 \text{ min}^{-1}$; sample uptake rate $1.0 \text{ cm}^3 \text{ min}^{-1}$, controlled by peristaltic pump; concentric glass nebulizer (type B, Meinhard).

A double-beam atomic absorption spectrometer, model 380 (Perkin—Elmer) was used with radiation sources: hollow cathode lamps (Cu, Cr), electrodeless lamps (Pb, Cd, Zn), with standard one-slot burner with acetylene—air flame and pneumatic nebulizer (uptake rate $7.5 \text{ cm}^3 \text{ min}^{-1}$).

The wavelengths of spectral lines used at the measurement by the OES-ICP and by the AAS are listed in Table 1.

Table 1
Measured spectral lines

Element	λ/nm	
	OES-ICP	AAS
Cd	214.438*	228.80
Cr	205.552*	357.87
Cu	324.754	324.75
Pb	220.353*	283.31
Zn	213.856	213.96

* Ion lines.

Basic solutions were prepared in concentration $\rho = 1 \mu\text{g cm}^{-3}$ of the given element (Pb in concentration $10 \mu\text{g cm}^{-3}$) from the following compounds: CdSO_4 , K_2CrO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and ZnSO_4 . All reagents were of anal. grade purity. The referred concentrations of the investigated elements were chosen so that the precision of their determination expressed by the relative standard deviation was for each element less than 1% [25].

The measured solutions were adjusted with the addition of concentrated acids (anal. grade purity): HNO_3 (65%), HCl (37%), H_2SO_4 (96%), and H_3PO_4 (85%) in volume V/cm^3 : 0.5, 1.0, 5.0, 10.0, 20.0, and 50.0 in 100 cm^3 of solution.

The following samples were analyzed: Czechoslovak attested reference material 1-03-010 zinc concentrate (Banská Štiavnica; w_i : 50.29% Zn, 9.68% Fe, 0.35% Cd, 0.58% Cu) and Czechoslovak attested reference material 1-01-016 pyrite concentrate (Banská Štiavnica; w_i : 38.96% Fe, 0.73% Pb, 2.49% Zn, 7.25% SiO_2 , 0.32% Cu), products of the Institute for Ore Research, Prague.

Sample decomposition

Sample (5 g) was treated with concentrated HCl (50 cm^3), after addition of KClO_3 solution (5%, 1 cm^3) and boiling of the mixture another 1 cm^3 of the KClO_3 solution was

added. After the removal of chlorine by its boiling off, 10 % KI (2 cm^3) was added, filtered and brought to 500 cm^3 by redistilled water.

For the analysis 25 cm^3 of the sample solution and 2.5 cm^3 of concentrated HCl, resp. HNO_3 , H_2SO_4 or H_3PO_4 were added into four beakers. The solutions containing different acids were evaporated on water bath practically to dryness, 2.5 cm^3 of the corresponding concentrated acid were again added and the volume was brought to 100 cm^3 by redistilled water. The prepared solutions contained 5 cm^3 of different concentrated acids in 100 cm^3 of solution.

Results and discussion

The presence of mineral acids in analyzed solutions causes a depression of the spectral line intensity of measured elements. The depression is manifested on spectral lines of both, atomic and ionic character.

The depression of spectral line intensity can be caused by a lowered analyte concentration in plasma resulting from changes in density and viscosity of the measured solutions evoked, as compared with aqueous solutions, by different contents of mineral acids. These changes can be partly eliminated by ensuring a constant volume supply of the sample to the nebulizer [9, 14]. We therefore worked only with the use of peristaltic pump.

The presence of mineral acids in analyzed solutions gives rise to different effects occurring in the plasma, resulting in the majority of cases in a depressive influence on the spectral line intensity of different elements. Many interferences are influenced *e.g.* by the type and construction of generators. It was found that acid interferences are manifested more at instruments having generators working on frequencies about 50 MHz and less at ones working with the frequency of 27.12 MHz [26, 27].

Till the recent time a quantitative expression of acid interferences or a full compensation of their different demonstrations by simple changes of experimental conditions has not been possible. The use of internal reference elements has also not been able to eliminate various interferences of acids. It therefore was necessary to perform a quantitative evaluation of interferences caused by different mineral acids and to study the possibilities of their elimination using the given experimental arrangement and special working conditions.

Different acid interferences (mainly of depressive character) are connected also with the lowering of the plasma temperature caused by energy losses corresponding to the atomization of acid molecules [26, 27].

We solve the problem of elimination of acid interferences. The graphical presentation of axial profile scans of spectral line intensity (Fig. 1) shows that the maximum intensity depression with the growing acid content is observed at the most commonly used observation height corresponding to the maximum

signal to background ratio (SBR) resulting in the best detection limit, whereas the wings of the mentioned profiles are less interfered. We used this fact and worked at observation height at which the differences between the observed axial profiles of spectral line intensities are lower (h optimized). This procedure enables so a partial elimination of acid interferences as shown for Cu in Fig. 2.

In the case of copper, the correction procedure gives acceptable results for the addition of concentrated HCl, HNO₃, and H₃PO₄ to 20 cm³, resp. 10 cm³ H₂SO₄ in 100 cm³ of the analyzed solutions.

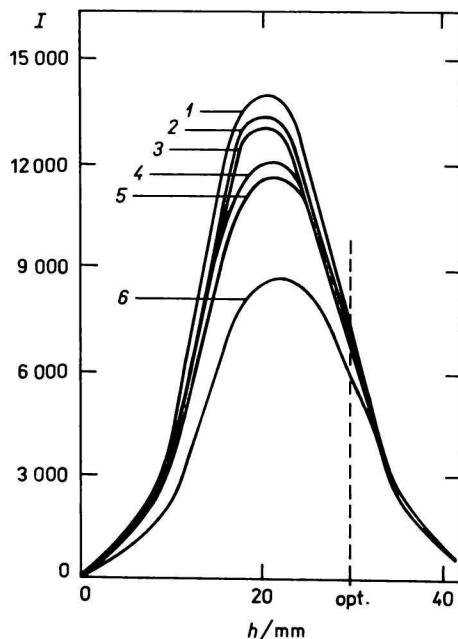


Fig. 1. Influence of the HNO₃ content on the axial intensity profile of the spectral line with $\lambda(\text{Cu}) = 324.754 \text{ nm}$ at observation height h . $V(\text{conc. HNO}_3)/\text{cm}^3$ in 100 cm³ of solution: 1. 0.5, 2. 1, 3. 5, 4. 10, 5. 20, 6. 50. $\rho(\text{Cu}) = 1 \mu\text{g cm}^{-3}$

For cadmium the interference of HCl, HNO₃, and H₃PO₄ can be eliminated by the optimization of the observation height to the volume of 10 cm³ of concentrated acid in 100 cm³ of the final solution. For higher acid contents only partial effect can be achieved (the depression is lowered by 8–10 % as compared with the measurement at the observation height corresponding to the max. SBR). For higher contents of H₂SO₄ the procedure is unsuitable.

At the determination of chromium the interference of HCl, HNO₃, and H₃PO₄ can be practically eliminated by the change of the observation height to the acid content of 10 cm³ in 100 cm³. At higher acid contents the depressive influence is lowered by 10–15 % as compared with the measurement at the max. SBR. For solutions containing H₂SO₄ the procedure is unsuitable.

The influence of acid concentration on the related intensity of the investigated Pb spectral line shows only a small efficiency of the correction procedure. For amounts of concentrated acids higher than 20 cm³ in 100 cm³ of solution the improvement corresponds to about 5 %.

In the case of zinc the greatest spectral line intensities can be found, unlike to the other investigated elements, with addition of HNO₃ and not HCl. By the change of the observation height the depressive influence of acids can be lowered for volumes of HCl and H₃PO₄ higher than 10 cm³ in 100 cm³ of solution by 10–20 %.

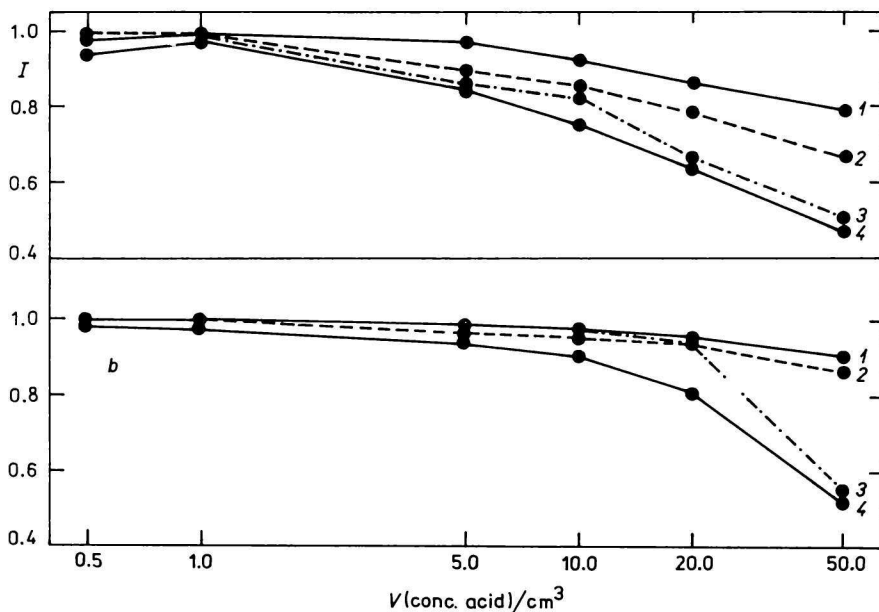


Fig. 2. Influence of the added amount of acid (in 100 cm³ of solution) on the intensity of the spectral line with $\lambda(\text{Cu}) = 324.754 \text{ nm}$ at the observation height corresponding to max. SBR (a) and at the optimized observation height (b).

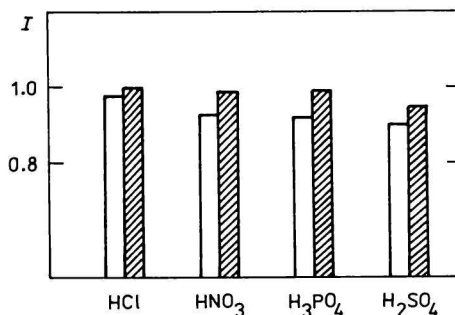
1. HCl; 2. HNO₃; 3. H₃PO₄; 4. H₂SO₄.

The obtained graphical dependences of related intensities of the investigated spectral lines on the added content of one type of acid show that up to the addition of 5 cm³ of any used concentrated acid in 100 cm³ of the solution (except H₂SO₄) no significant change in the signal value is caused. The intensities are related to the spectral line intensity measured in the solution containing 5 cm³ of concentrated HCl in 100 cm³ which value is taken as equal to one. The interference of different acids (5 cm³ in 100 cm³) is presented for Cu in Fig. 3.

Similar situation was found also for Cd, Cr, Pb, and Zn. The presented results were obtained with model solutions (one element in one acid).

The depression of the intensities in the presence of mineral acids was observed on spectral lines of atomic and ionic character of the investigated elements. At the same addition of concentrated acids their depressive influence ranges as follows: HCl, HNO₃, H₃PO₄, H₂SO₄ (for Zn: HNO₃, HCl, H₃PO₄, H₂SO₄). This experimental result is in accordance with other published statements [9, 10, 14, 26, 27] but the quantitative evaluation of the observed interferences depending on several factors, as listed in the introduction, is different. Owing to the fact that the quantitative level of mineral acid interferences depends also on the used instrumentation (type of generator, optics, nebulizer, *etc.*) it is necessary to perform their investigations separately for each experimental arrangement.

Fig. 3. Bar diagrams of related intensities ($\lambda(\text{Cu}) = 324.754 \text{ nm}$) in different acids (5 cm^3 of concentrated acid in 100 cm^3 of solution) at the observation height corresponding to max. SBR \square and at the optimized observation height ▨



In order to check the reliability of the discussed procedure enabling the elimination of acid interferences, in the following part of the paper we applied the gained results to the analysis of real samples.

In the first case the prepared solutions contained 5 cm^3 of different concentrated acids in 100 cm^3 of solution and were analyzed by AAS and OES-ICP (at the optimized observation height) using calibration solutions prepared with the same addition of hydrochloric acid. The results are in Tables 2 and 3. On the basis of these results it is possible to conclude that the presence of 5 cm^3 of concentrated HCl, HNO₃, and H₃PO₄ in 100 cm^3 of the solution corresponding also to real samples does not cause any significant depression of spectral line intensities and consequently, for the determined elements any deterioration of the accuracy of the gained results. As a consequence of restricted solubility of corresponding salts, in the case of H₃PO₄ and H₂SO₄ additions, considerably lower values for Pb, as compared with HCl and HNO₃, were found.

Using the same calibration solutions (*i.e.* 5 cm^3 of concentrated HCl in 100 cm^3) the above-mentioned attested reference materials containing an addi-

Table 2

Czechoslovak attested reference material 1-03-010 zinc concentrate

Addition 5 cm ³	w(Cd)/%		w(Cu)/%		w(Pb)/%	
	AAS	OES-ICP	AAS	OES-ICP	AAS	OES-ICP
HCl	0.34	0.34	0.57	0.56	1.50	1.50
HNO ₃	0.34	0.34	0.58	0.56	1.52	1.50
H ₃ PO ₄	0.32	0.32	0.57	0.56	0.50	0.45
H ₂ SO ₄	0.31	0.31	0.55	0.54	0.14	0.14
Recommended value	0.35 %		0.58 %		—	

Table 3

Czechoslovak attested reference material 1-01-016 pyrite concentrate

Addition 5 cm ³	w(Zn)/%		w(Cu)/%		w(Pb)/%	
	AAS	OES-ICP	AAS	OES-ICP	AAS	OES-ICP
HCl	2.48	2.48	0.31	0.30	0.73	0.72
HNO ₃	2.48	2.50	0.31	0.30	0.71	0.72
H ₃ PO ₄	2.45	2.45	0.29	0.28	0.40	0.40
H ₂ SO ₄	2.47	2.26	0.26	0.26	0.18	0.20
Recommended value	2.49 %		0.32 %		0.73 %	

Table 4

Czechoslovak attested reference material 1-03-010 zinc concentrate

Addition 20 cm ³	w(Cd)/%		w(Cu)/%		w(Pb)/%	
	max. SBR	<i>h</i> opt.	max. SBR	<i>h</i> opt.	max. SBR	<i>h</i> opt.
HCl	0.30	0.34	0.50	0.56	1.40	1.52
HNO ₃	0.30	0.32	0.50	0.56	1.40	1.50
H ₃ PO ₄	0.27	0.30	0.49	0.54	0.27	0.27
H ₂ SO ₄	0.20	0.20	0.40	0.40	0.10	0.10
Recommended value	0.35 %		0.58 %		1.5 % ^a	

a) Value of AAS.

tion of 20 cm³ of concentrated acid in 100 cm³ of solution were also analyzed. The results are in Tables 4 and 5. As proved by model solutions, at this acid content already considerably lower spectral line intensities were found. In spite of that fact it can be stated that the differences between the recommended values and results obtained by the measurement at the observation height optimized for the suppression of acid interferences are lower than in the case when the

Table 5

Czechoslovak attested reference material 1-01-016 pyrite concentrate

Addition 20 cm ³	w(Zn)/%		w(Cu)/%		w(Pb)/%	
	max. SBR	<i>h</i> opt.	max. SBR	<i>h</i> opt.	max. SBR	<i>h</i> opt.
HCl	1.86	2.22	0.25	0.30	0.61	0.70
HNO ₃	2.00	2.38	0.23	0.29	0.62	0.72
H ₃ PO ₄	1.70	2.02	0.20	0.26	0.30	0.40
H ₂ SO ₄	1.20	1.33	0.18	0.18	0.08	0.12
Recommended value	2.49 %		0.32 %		0.73 %	

measurements were performed at the observation height corresponding to the max. SBR, leading to the best detection power. It means that the acid interference can partly be eliminated by this procedure also at such extreme conditions. It is true that the procedure causes a deterioration of the detection power which circumstance however does not play any primary role, if accurate determination of concentrations the values of which considerably surpass detection limits is claimed.

Conclusion

Experimentally determined suitable observation height enables to correct in a given extent interferences of different matrices (HCl, HNO₃, H₃PO₄, but H₂SO₄ only in some cases, *e.g.* for Cu), as well as of different concentrations of acids present in analyzed solutions. Consequently, samples containing an addition of some of the investigated acids can be after a suitable choice of observation height analyzed with the use of calibration solutions prepared in another acid.

To obtain accurate results, the sample preparation (decomposition of solid samples and following treatment) has to be performed so, lest the analyzed solution should contain more than 10 cm³ of concentrated acid in 100 cm³

The presented procedure for the elimination of acid interferences has no special claims on the duration of analyses and needs neither supplemental treatment of samples, nor simulation of basic composition and it makes possible to analyze samples prepared in different manner using just one set of calibration solutions.

References

1. Greenfield, S., Jones, I. L., and Berry, C. T., *Analyst* (London) 89, 713 (1964).
2. Fassel, V. A. and Kniseley, R. N., *Anal. Chem.* 46, 110A and 1155A (1974).

3. Fassel, V. A., *Proc. 16th Coll. Spectrosc. Int. Heidelberg 1971, Plenary Lectures and Reports*, p. 63. Hilger, London, 1972.
4. Boumans, P. W. J. M., de Boer, F. J., Dahmen, F. T., Noelzel, H., and Meier, A., *Spectrochim. Acta*, **B30**, 449 (1975).
5. Boumans, P. W. J. M. and de Boer, F. J., *Spectrochim. Acta*, **B31**, 355 (1976).
6. Mermet, J. M. and Robin, J. P., *Anal. Chim. Acta* **75**, 271 (1975).
7. Mermet, J. M., *Spectrochim. Acta*, **B30**, 383 (1975).
8. Larson, G. F., Fassel, V. A., Scott, R. H., and Kniseley, R. N., *Anal. Chem.* **47**, 238 (1975).
9. Maessen, F. J. M. J., Balke, J., and de Boer, J. L. M., *Spectrochim. Acta*, **B37**, 517 (1982).
10. Kawaguchi, H., Ito, T., Ota, K., and Mizuika, A., *Spectrochim. Acta*, **B35**, 199 (1980).
11. Greenfield, S., McGeachin, M. D., and Smith, P. B., *Anal. Chim. Acta* **84**, 67 (1976).
12. Koirtzjohann, S. R., Jones, J. S., Jester, C. P., and Yates, D. A., *Spectrochim. Acta*, **B36**, 49 (1981).
13. Blades, M. W. and Horlick, G., *Spectrochim. Acta*, **B36**, 881 (1981).
14. Dahlquist, R. L. and Knoll, J. W., *Appl. Spectrosc.* **32**, 1 (1978).
15. Thompson, M., Ramsey, M. H., and Coles, B. J., *Analyst* (London) **107**, 1286 (1982).
16. Myers, S. A. and Tracy, D. H., *Spectrochim. Acta*, **B38**, 1227 (1983).
17. Greenfield, S., *Developments in Atomic Plasma Spectrochemical Analysis*. (Barnes, R. M., Editor.) P. 1. Heyden, London, 1981.
18. Salin, E. D. and Horlick, G., *Anal. Chem.* **52**, 1578 (1980).
19. Lorber, A., Goldbart, Z., and Eldan, M., *Anal. Chem.* **56**, 43 (1984).
20. Lorber, A. and Goldbart, Z., *Anal. Chem.* **56**, 37 (1984).
21. Kalivas, J. H. and Kowalski, B. R., *Anal. Chem.* **54**, 560 (1982).
22. Botto, R. J., *Spectrochim. Acta*, **B40**, 397 (1985).
23. Plško, E., *Proc. 30th Hungarian Annual Conference on Spectral Analysis*, p. 21. Debrecen, 1987.
24. Plško, E., *Vybrané metody analytické atomové spektroskopie*. (Selected Methods of Analytical Atomic Spectroscopy.) P. 209. Czechoslovak Spectroscopic Society, Prague, 1987.
25. Kubová, J. and Streško, V., *Hydrochémia* **87**, p. 173. Slovak Water-Economical Society, Bratislava, 1987.
26. Chudinov, E. G. and Varvanina, G. V., *Zh. Anal. Khim.* **44**, 5 (1989).
27. Chudinov, E. G. and Varvanina, G. V., *Zh. Anal. Khim.* **44**, 814 (1989).

Translated by E. Plško