Asian Journal of Chemistry Vol. 17, No. 3 (2005), 1518–1526

Matrix Effects of Concomitant Species on the Determination of Nickel by Inductively Coupled Plasma Atomic Emission Spectrometry

OSMAN AKBA*, AKIN BAYSAL, MELEK MERDIVAN†, CANDAN HAMAMCI
and BAHATTIN GUMGUM
Department of Chemistry, Faculty of Sciences and Arts
Dicle University, TR- 21280 Diyarbakir, Turkey
Fax: (90)(412) 2488389: E-mail: oakba@dicle.edu.tr

The interference on the determination of nickel by the salts LiCl, NaCl, KCl, CsCl, NH_4Cl, Na_2SO_4, $NaNO_3$, $NaC_2H_3O_2$ in an inductively coupled plasma-atomic emission spectrometry has been carried out. The salt concentration was in the 100–10000 mg L^{-1} range. Nickel emission was enhanced at lower matrix concentrations (100 mg L^{-1}) and was depressed at higher matrix concentrations (10000 mg L^{-1}). Except cesium, above 100 mg L^{-1}, all studied ions caused a decrease in the signal intensity in the range of 0–15%. The sequence order of the investigated ions for the enhancement and depression was unstable. The sequence order in enhancement was found as $Li^+ < Na^+ < K^+ < Cs^+ < NH_4^+$ for cation; $NO_3^- < SO_4^{2-} < Cl^- < OAc^-$ for anions and $Cs^+ < NH_4^+ < K^+ < Li^+ < Na^+$ for cations and $OAc^- < SO_4^{2-}$, $Cl^- < NO_3^-$ for anions in depression at the studied lines.

Key Words: Matrix Effect, Concomitant Species, Nickel, ICP-AES.

INTRODUCTION

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been widely used for quantitative analysis because of its ease of use, its multi-element capability and its low limits of detection. Although interferences in ICP-AES are less severe than other techniques such as flame atomic absorption spectrometry, matrix problems can take place and affect the analytical results in terms of accuracy and precision. Matrix interference effects are caused by the components of the sample solution other than the analyte and result in increased or decreased analyte emission. Among matrix effects, the effects of inorganic acids[1–8] and organic acids[9–13] as the dissolution reagents and easily ionized elements[14–34] as a natural matrix in ICP-AES have been widely studied depending on their quantification, dependence on operating conditions and reduction strategies.

Ionization interferences caused a change in the ionization equilibrium of the analyte due to the presence of an easily ionized element in the plasma. There are conflicting reports concerning the observation of matrix effect in ICP-AES[23–34]. At identical operating conditions, detection limits in strong salt solutions tend to be superior to those measured from pure aqueous solutions for two different

---

†Department of Chemistry, Faculty of Sciences and Arts, Dokuz Eylul University, TR-35160 İzmir, Turkey.

reasons. First, the sensitivity of the analyte may be lower because of a matrix effect in the ICP resulting from the concomitant salt. Second, the baseline was not stable because of increased noise and background shift by the salt solution to an extent depending on the nebulizer type[1, 14, 21, 31].

The present work describes the effects of the concomitants on the analytical signal of nickel by ICP-AES. These studied ions, which are the most common constituents of naturally occurring samples, severely interfere in the spectrochemical determination of the analyte. The determination of nickel having constant concentration (10 mg L^{-1}) in ICP-AES was studied for a representative selection of spectral lines in the presence of a matrix containing growing concentrations of studied ions.

EXPERIMENTAL

A Jobin Yvon 24 ICP-AES was used throughout the experiments. Specification of the spectrometer, operating conditions and studied optical wavelengths are shown in Table-1. Plasma and carrier gas, flow rates and observation heights were not changed during the experiment. Although interference effects can be expected to vary according to operating parameters, a single set of conditions was chosen to approximate those typically used for normal analytical work. These conditions were held constant throughout the study.

TABLE-1
INSTRUMENTATION AND OPERATING CONDITIONS FOR ICP-AES

Instrument	
Spectrometer	JY24 (Jobin Yvon-sequential)
Generator	40.68 MHz, 1 kW
Operating conditions:	
Plasma gas	JY24 (Jobin Yvon-sequential)
Sheathing gas	Argon, 0.52 L/min
Nebulizer gas	Argon, 0.30 L/min, 3.0 bars
Nebulizer	Meinhard, Type C-0.5
Torch	JY Ryton, demontable quartz teflon system
PMT tube	160–180 nm
Observation height	
Integration time	
Monochromator	HR 640, 2400 g/mm, 64 cm focus, resolution: 0.01 nm
Wavelengths	**nm**
Ni(II)	217.467
Ni(II)	225.386
Ni(II)	227.021
Ni(II)	230.000
Ni(II)	239.452
Ni(I)	234.554

Lithium, sodium, potassium, cesium and ammonium solutions as chloride salts and sulfate, nitrate, chloride and acetate as sodium salts were prepared from analytical reagent grade salts in doubly distilled water. Commercial optical emission standard for nickel (SPEX Plasma Standard 1000 μg mL^{-1}, Metuchen, USA) was used to prepare the standard and working solutions. Solutions of 100, 1000, 10000 μg mL^{-1} concentrations of the salts were prepared from their stock solutions and then spiking with a 1000 μg mL^{-1} Ni standard solution as to contain a final solution Ni concentration of 10 μg mL^{-1}. Ultrapure water 18.2 mΩ specific resistivity was obtained from the Milli-Q system of Millipore Corporation.

Each test solution was measured as an average of 10 times line signals. Background subtraction was made using the signal on either side of the emission line as the background.

RESULTS AND DISCUSSION

Matrix effects are likely to be troublesome in the analysis of nickel materials, in either a geochemical or metallurgical context. Matrix effects due to alkali metal ions such as Li^+, Na^+, K^+, Cs^+ and NH_4^+ ion and anions as NO_3^-, SO_4^{2-}-, Cl^- and OAc^- were studied in the analysis of nickel by measuring analyte signals from solutions containing various concentrations of these interfering ions under robust plasma conditions. The matrix interference from an interfering ion/analyte ratio of 10 : 1 up to 1000 : 1 was observed by holding Ni concentration at 10 mg L^{-1}. All studied ions usually showed a more or less depressing effect on the emission intensities of the studied analytical lines above an interferent to analyte (I/A) ratio of 10.

For lithium, up to I/A ratio of 100, interference effect was positive, but at the I/A ratio of 10 enhancement was slightly higher as shown in Fig. 1. Depression effect was larger at a ratio of 1000 and became negative. The less affected analytical line was 225.386 nm. The interference trend from Na showed similarity

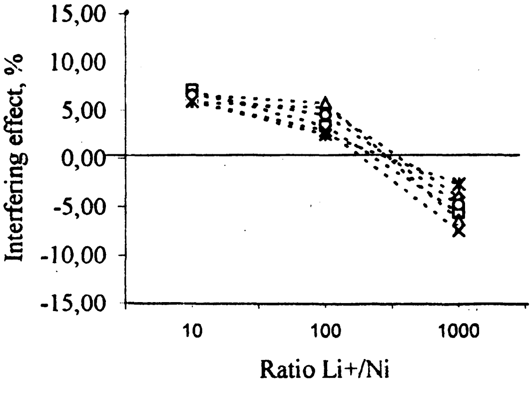

Fig. 1. Forms of interference of lithium on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (– □ –) 234,554 nm, (– Δ –) 230,300 nm, (– × –) 227,021nm, (– ✳ –) 225,386 nm, (– O –) 217,467nm

with Li (Fig. 2). The enhancement at I/A ratio of 10 and the depression above this ratio were high. Interference effect was lowest at 239.452 and 234.554 nm and highest at 225.386 and 227.011 nm at the highest ratio. The interference effect of potassium on nickel was lowest at a ratio of 100 at two analytical lines as given in Fig. 3. The decreasing level at a high interferent-analyte ratio of 1000 was lower than Li^+, Na^+ and NH_4^+ ions. Potassium has a negligible effect on the determination of nickel at 225.386 nm. The interference effect of cesium on nickel was seen as enhancement within the range of 1–10% in spite of being depression by increasing the interferent/analyte ratio. The degree of decreasing in the emission intensity of nickel from cesium at all studied lines was lowest within all studied ions (Fig. 4). On the contrary, the increase in the concentration of interferent caused differentiation in the depression trend of cesium at two lines; the highest enhancement at 227.021 nm and the lowest enhancement at 225.386

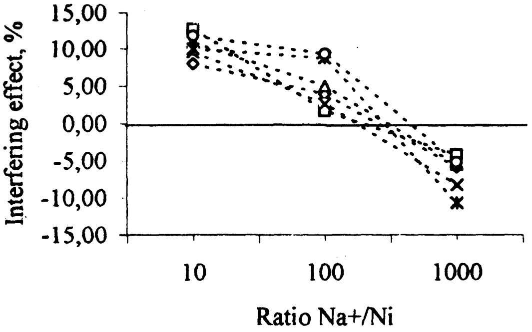

Fig. 2. Forms of interference of sodium on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm, (– × –) 227,021nm, (– ⁎ –) 225,386 nm, (– O –) 217,467nm

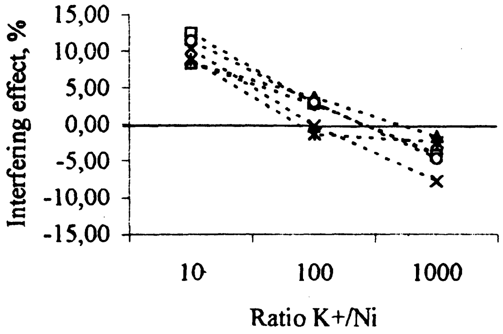

Fig. 3. Forms of interference of potassium on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm, (– × –) 227,021nm, (– ⁎ –) 225,386 nm, (– O –) 217,467nm

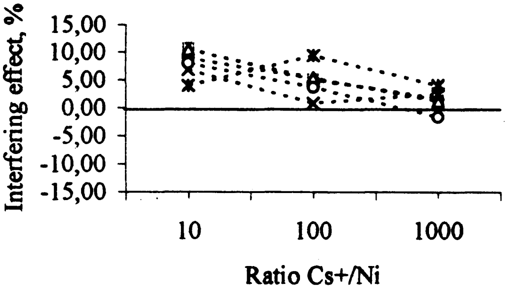

Fig. 4. Forms of interference of cesium on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– × –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

nm at the interferent to analyte ratio of 100. Ammonium ion showed the strongest interference for nickel determination at all investigated lines at the I/A ratio of 10 and 100 and the increase in intensity was about the range of 5 to 20% (Fig. 5). At the highest I/A ratio of 1000, the depression caused a decrease in emission intensity up to *ca.* 10% at all lines except 230.000 and 217.467 nm. The 225.386 nm at I/A ratio of 100 and 227.021 and 234.554 nm at I/A ratio of 1000 were the less affected emission lines of nickel.

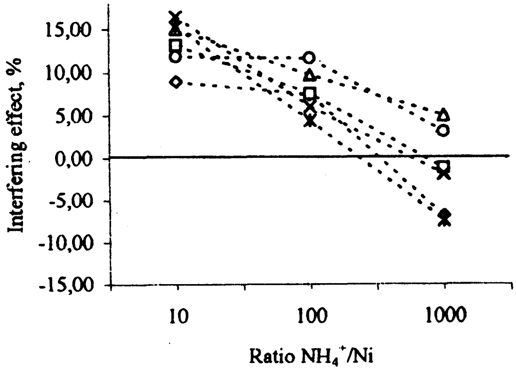

Fig. 5. Forms of interference of ammonium ion on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– × –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

The trends of interferences from SO_4^{2-}, Cl^- and OAc^- ions were similar except NO_3^- ion. The strong depression effect of nitrate ion on the determination of nickel for all studied lines caused a decrease in intensity of emission up to *ca.* 15% at an interfering/analyte ratio of 100 and 1000 (Fig. 6). The interference observed at the lowest ratio has been negligible for all lines. As shown in Fig. 7, the effect of SO_4^{2-} at I/A ratio of 10 and 100 was similar and enhances the intensity up to

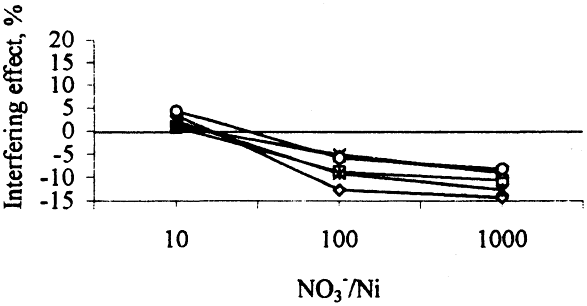

Fig. 6. Forms of interference of nitrate ion on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– × –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

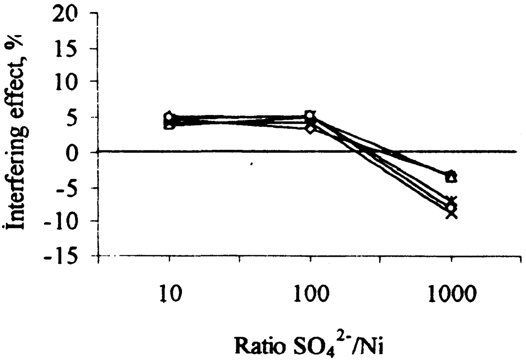

Fig. 7. Forms of interference of sulphate ion on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– × –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

5% for all investigated lines. At the highest ratio, the observed depression was large and the decreasing ratio in the signal intensity was around 12. At 239.452 and 234.554 nm, the intensity of analytical signal was affected partly at all ratios. The interference trend of chloride ion was similar to sulphate and acetate ions but decrease in the line intensities was lower than OAc^- and higher than SO_4^{2-} ion (Fig. 8). The change in the intensity of analytical signal from I/A ratio of 100 to 1000 was high as shown in SO_4^{2-} effect. The acetate ion caused the enhancement at the interferent/analyte ratio of 10 and 100 as represented in Fig. 9. The increase in the intensities at the studied lines was highest within all investigated ions at the lowest I/A ratio, 10. The less affected line from OAc^- was 217.467 nm. The depression effect was almost high from 10 to 100 I/A ratio, approximately for all lines.

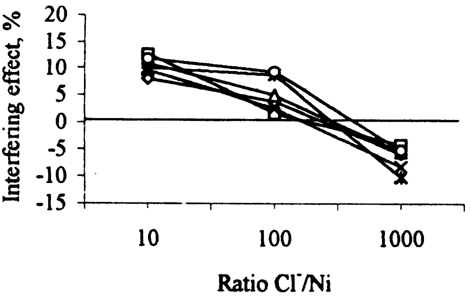

Fig. 8. Forms of interference of chloride ion on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– x –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

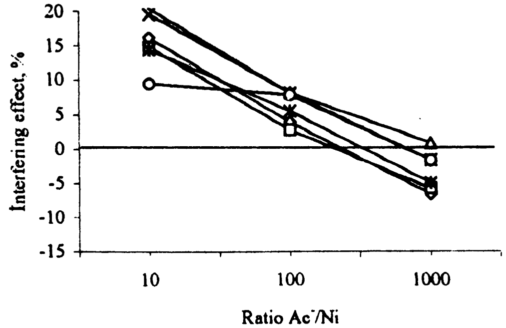

Fig. 9. Forms of interference of acetate" ion on nickel at studied analytical lines.
Symbols: (– ◊ –) 239,452 nm (–□–) 234,554 nm, (– Δ –) 230,300 nm,
(– x –) 227,021nm, (– ✱ –) 225,386 nm, (– O –) 217,467nm

Interferences that take place during the volatilization-atomization process affect the emission of both atoms and differences in energy transfer caused by sample concomitants. In general, the addition of an alkali or ammonium and anion matrix elements enhanced emission signal intensity in the lower concentrations for the studied wavelengths in the determination of nickel. In the lower matrix concentration, the mechanism causing an enhancement appears to be the result of increased collisional excitation, as a result of an increase in the number of electrons with the appropriate energy to cause excitation of atom or ion levels. In the higher matrix concentration, emission intensity depressed. As the effects of increased excitation decrease with higher matrix concentration, the influence of ambipolar diffusion begins to exert an influence on the spatial distribution of analyte species. This eventually leads to observed depressions in the analyte emission intensity. In addition, changing in nebulizer efficiency and droplet size distribution and changing aerosol transport efficieny at high salt concentrations may also contribute to the variation at nickel analytical signal intensity.

The matrix element of cesium having lowest ionization potential produces the largest enhancement effect on nickel emission. The interference from either the alkali elements, ammonium ion or anions is seen as whether enhancement or depression was much similar for almost all investigated lines at studied robust plasma. The change in line intensity was correlated with the excitation energy. The interference trends were found to be in the order of $NH_4^+ > Cs^+ > K^+ > Na^+ > Li^+$ and $OAc^- > Cl^- > SO_4^{2-} > NO_3^-$ in enhancement and $Na^+ > Li^+ > K^+ > NH_4^+ > Cs^+$ and $NO_3^- > Cl^-, SO_4^{2-} > OAc^-$ in depression. The interference effect of alkali elements on the determination of nickel is similar to the previous studies concerning transition elements and rare earth elements[13, 15, 16, 26, 35–39]. Also, the suppression trend of Na, K, Li and Cs is the same as given in literature[26]. The specific emission line for determination of nickel in concomitant salts by ICP-AES could not be proposed due to obtained similar interfering effects. But, at all lines, the change in intensity of nickel emission was only around ±15–20% and this effect may be overcome by the internal standardization or matrix-matching technique.

REFERENCES

1. A. Fernandez, M. Murillo, N. Carrion and J.M. Mermet, *J. Anal. At. Spectrom.*, **9**, 217 (1994).
2. I.I. Stewart and J.W. Olesik, *J. Anal. At. Spectrom.*, **13**, 843 (1998).
3. B. Gumgum and C. Hamamci, *J. Quant. Spectrosc. Radiat. Transfer*, **50**, 55 (1993).
4. A. Canals, L. Gras and H. Contreras, *J. Anal. At. Spectrom.*, **17**, 219 (2002).
5. M. Murillo, R. Amaro and A. Fernandez, *Talanta*, **60**, 1171 (2003).
6. M. Grotti, R. Leardi and R. Frache, *Spectrochim. Acta*, **57B**, 1915 (2002).
7. J. Mora, L. Gras, E.H. Van Veen and M.T.C. de Loos-Vollebregt, *Spectrochim. Acta*, **54B**, 959 (1999).
8. J.L. Todoli, J.M. Mermet, A. Canals and V. Hernandis, *J. Anal. At. Spectrom.*, **13**, 55 (1998).
9. J. Xu, H. Kawaguchi and A. Mizuike, *Anal. Chim. Acta*, **152**, 133 (1983).
10. R.M. Belchamber, D. Betteridge, A.P. Wade, A.J. Cruickshank and P. Davison, *Specrochim. Acta*, **41B**, 503 (1986).
11. S. Roncevic and M. Siroki, *J. Anal. At. Spectrom.*, **9**, 99 (1994).
12. T.D. Hettippathirana, A.P. Wade and M.W. Blades, *Spectrochim. Acta*, **45B**, 27 (1990).
13. C. Dubuisson, E. Poussel and J.M. Mermet, *J. Anal. At. Spectrom.*, **13**, 1265 (1998).
14. L.M. Faires, C.T. Apel and T.M. Niemczyk, *Appl. Spectrosc.*, **37**, 558 (1983).
15. J.A. Olivares and R.S. Houk, *Anal. Chem.*, **58,** 20 (1986).
16. A. Mazzucotelli, F. Paz, E. Magi and R. Frache, *Anal. Sci.*, **8**, 189 (1992).
17. M. Grotti, C. Ianni and R. Frache, *Talanta*, **57**, 1053 (2002).
18. A. Krejova, T. Cernohorsky and E. Curdova, *J. Anal. At. Spectrom.*, **16**, 1002 (2001).
19. M. Grotti, E. Magi and R. Frache, *J. Anal. At. Spectrom.*, **15,** 89 (1999).
20. I.B. Brenner, A. Zander, M. Cole and A. Wiseman, *J. Anal. At. Spectrom.*, **12**, 897 (1997).
21. X. Romero, E. Poussel and J.M. Mermet, *Spectrochim. Acta*, **52B**, 495 (1997).
22. N.N. Sesi and G.M. Hieftje, *Spectrochim. Acta*, **51B**, 1601 (1996).

23. M.H. Abdallah, J.M. Mermet and C. Trassy, *Anal. Chim. Acta*, **84**, 238 (1976).
24. P.W.J.M. Bounmans and F.J. De Boer, *Spectrochim. Acta*, **31B**, 355 (1976).
25. G.R. Kornblum and L.De Galan, *Spectrochim. Acta*, **32B**, 455 (1977).
26. M.W. Blades and G. Horlick, *Spectrochim. Acta*, **36B**, 881 (1981).
27. W.H. Gunter, K. Visser and P.B. Zeeman, *Spectrochim. Acta*, **37B**, 571 (1982).
28. R. Rezaaiyaan and G.M. Hieftje, *Anal. Chem.*, **57**, 412 (1985).
29. L.J. Prell, C. Monning, R.E. Harris and S.R. Koirtyohann, *Spectrochim. Acta*, **40B**, 1401 (1985).
30. G.D. Rayson and G.M. Hieftje, *Spectrochim. Acta*, **41B**, 683 (1986).
31. M.W. Blades and G. Horlick, *Spectrochim. Acta*, **36B**, 881 (1987).
32. M.R. Tripkovic and I.D. Holclajtner-Antunovic, *J. Anal. At. Spectrom.*, **8**, 349 (1993).
33. H. Kawaguchi, T. Ito, K. Ota and A. Mizuike, *Spectrochim. Acta*, **35B**, 199 (1980).
34. G. Rezaaiyaan, J.W. Olesik and G.M. Hieftje, *Spectrochim. Acta*, **40B**, 73 (1985).
35. R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray and C.E. Taylor, *Anal. Chem.*, **52**, 2283 (1980).
36. H.R. Date and A.L. Gray, *Analyst*, **106**, 1255 (1981).
37. B. Budic, *Fresenius J. Anal. Chem.*, **368**, 371 (2000).
38. C. Dubuisson, E. Poussel and J.M. Mermet, *J. Anal. At. Spectrom.*, **12**, 897 (1997).
39. I.B. Brenner, A. Le Marchand, C. Daraed and L. Chauvet, *Microchem. J.*, **63**, 344 (1999).

(*Received*: 26 July 2004; *Accepted:* 14 March 2005) AJC-4130