Available online at www.sciencedirect.com

International Journal of Mass Spectrometry 226 (2003) 271–278

www.elsevier.com/locate/ijms

Formation of polyatomic ions from the skimmer cone in the inductively coupled plasma mass spectrometry

N.F. Zahran, A.I. Helal*, M.A. Amr, A. Abdel-Hafiez, H.T. Mohsen

Center Laboratory for Elemental and Isotopic Analysis, Atomic Energy Authority, Cairo 13759, Egypt

Received 29 July 2002; accepted 13 January 2003

Abstract

The inductively-coupled plasma ion source for mass spectrometry is very sensitive for multielement analysis with detection limits down to sub part per trillion (ppt). Polyatomic ions which could be formed in the mass spectra may interfere in the analysis of some elements. Experimental conditions have great influences on the formation of polyatomic ions. The present work demonstrates that the skimmer materials (Au, Ag, Ni, Cu and Al) are participating in the formation of polyatomic ions. Heats of formation of polyatomic species formed from the skimmer materials such as: AuX, AgX, NiX, CuX and AlX, where X = Ar, O, N and H, are calculated by Gaussian program (G94W).

Keywords: ICP-MS; Sampler and skimmer materials; Heat of formation

1. Introduction

When the first commercial inductively-coupled plasma mass spectrometry were launched in the early 1980s, great hopes existed for interference-free analysis. However, even in the first publications on plasma mass spectrometry [1], a number of interferences were identified. Since then, many studies were carried out to identify, characterize, and to attenuate them [2–6]. Since the Debye length in the plasma medium ($1 - 0.1\,\mu m$) is much smaller than the diameter of the sampling orifice (1.1 mm), it is possible to have the plasma flow through at least the first orifice as bulk plasma. Furthermore, sampling orifice geometry can be such that thermal boundary layers can be small compared to orifice diameter, so that the plasma can be sampled adiabatically. If this can be done, and the expansion is sufficiently rapid to prevent recombination and reaction, then a truly representative sample of the ions in the ICP can be obtained. In the original work [7], this objective was not achieved. With the small sampling orifice used (approximately 0.1 mm) a cooled boundary layer was formed over the sampler, and the observed mass spectra corresponded to the ionic composition of this cooled layer rather than to that bulk plasma [1,8–10]. When attempts were made to use larger orifice diameters [11–15], an unanticipated problem resulted. A secondary discharge occurred at the orifice. This caused a very high photon noise level, producing ions of high kinetic energy and energy spread, and led to rapid erosion of the orifice. It was thought that the secondary discharge resulted from an electro-gasdynamic effect which lead

---

* Corresponding author. Fax: +20-202-469-1749.
E-mail address: aihelal@soficom.com.eg (A.I. Helal).

1387-3806/03/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S1387-3806(03)00023-X

to an increase in the electron density at the orifice. This secondary discharge was called a "pinch" effect [8–10]. Furthermore, Date and Gray [16] reported that the ICP interface with sampling orifice 0.5 mm and the first differentially pumped region operated at a pressure of 1 Torr reduce the "rate of expansion" through the sampler orifice and that this eliminate the "pinch", but later reported that some residual arcing may be present [17,18].

A number of experiments were carried out by Douglas and French [18] to investigate the origin of the secondary discharge. All of their observations [18] are consistent with arcing at the orifice being caused by a comparatively high RF potential difference between the plasma and the grounded sampler. The present work concentrates on the formation of polyatomic from the material of the skimmer. Stability of these polyion species is calculated as heats of formation and their ionic stability are observed by time.

2. Theoretical considerations

The calculation of the thermodynamic quantities in the Gaussian program is based on the simplest molecular models. The equation for the formation reaction of diatomic molecule is given as

$$X^\bullet + Y \rightarrow [XY]^+ . \qquad (1)$$

The enthalpy change, ΔH, for this reaction is calculated by subtracting the sum of the heat of formation, ΔH_f, values for the reactants from the sum of the heat of formation values of the products.

$$\Delta H = \sum \Delta H_f\ (\text{products}) - \sum \Delta H_f\ (\text{reactants}) \qquad (2)$$

In the present calculations, Hartree–Fock with the LANL2MB basis set are used to calculate ΔH^{298}, where

$$\Delta H^{298} = \Delta E^{298} + \Delta(PV), \qquad (3)$$

$$\Delta E^{298} = \Delta E_e^0 + \Delta(\Delta E_e)^{298} + \Delta E_v^0 + \Delta(\Delta E_v)^{298} + \Delta E_r^{298} + \Delta E_t^{298}, \qquad (4)$$

where the terms are defined as follows: ΔE_e^0 is the energy difference between products and reactants at 0 K, $\Delta(\Delta E_e)^{298}$ the change in the electronic energy difference between 0 and 298 K, ΔE_v^0 the difference between the zero-point energies of the products and reactants at (0 K), $\Delta(\Delta E_v)^{298}$ the change in the vibrational energy difference between 0 and 298 K, $\Delta E_r{}^{298}$ the difference in the rotational energies of the products and reactants, and $\Delta E_t{}^{298}$ is the translational energy change between the products and reactants. By using the calculated values of energy changes of products and reactants and the values of the heats of formation of the reactants, it is possible to calculate the heats of formation of the products.

3. Experimental

All measurements are performed using the high-resolution inductively-coupled plasma mass spectrometer (JMS-PLASMAX2). The highest resolving power of the machine is 12,000. With this resolution, interfered masses and element ions can be easily separated from each other if the required resolution is <12,000. The operating conditions are presented in Table 1.

4. Results and discussion

Extracting ions from the plasma into the vacuum system is critical in ICP-MS, because it depends

Table 1
Experimental conditions used in the measurements

Forward RF power	1200 W
Reflected RF power	<2 W
Coolant gas flow rate	14 l/min
Auxiliary gas flow rate	0.3 l/min
Nebulizer gas flow rate	0.77 l/min
Accelerating voltage	6 kV applied on the sampler and skimmer
Mass resolution ($m/\Delta m$)	300–10000
Detector mode	Analogue
Sampling depth	5 mm
Optimization	Maximum ion intensity of 100 ppb of $^{89}Y^+$
Blank solution	1% sub-boiling nitric acid

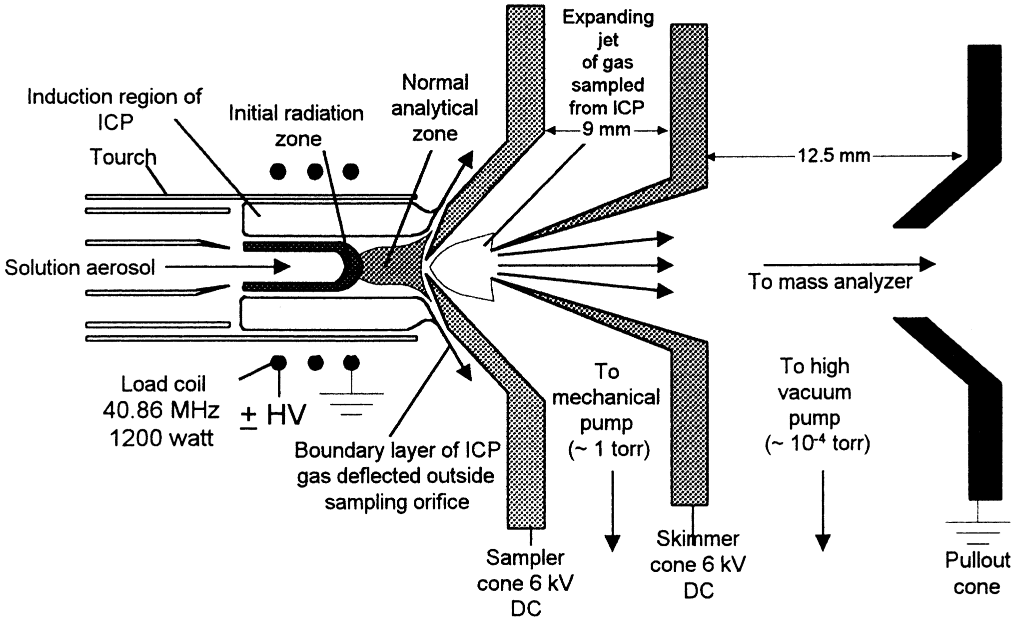

Fig. 1. Schematic diagram of ICP ion source of PLASMAX2 mass spectrometer.

mainly on the experimental conditions and the surrounding environment. A schematic diagram of plasma extraction interface of PLASMAX2 mass spectrometer is shown in Fig. 1. Ions flow through a sampling orifice (1.1 mm diameter in a cooled cone) into a mechanically pumped vacuum system, where a supersonic jet forms. The central section of the jet flows through the skimmer orifice (diameter = 0.9 mm). The extracted gas containing the ions attains supersonic velocities as it expands into the vacuum chamber and reaches the skimmer orifice in only few microseconds. The material of the sampler is changed, besides Cu sampler, to be from Au, Ag and Ni. Changing of the sampler material does not give any remarkable changes in the mass spectra. On the other hand, careful investigation of the effect of the skimmer cone shows that the skimmer materials greatly participate in the formation of polyatomic ions. The experimental process is proceeded in the way that the Cu sampler (which has no real effect on the formation of polyatomic ions) is used in all conditions while the material of the skimmer is changed to be, besides Cu, the coated Cu and Al skimmer. Cu skimmer is coated by Au by a coating unit, by Ag and Ni–Cr by chemical coating in solutions. The initial degree of coating is determined by scanning electron microscope equipped with energy dispersive X-ray spectrometer (EDS) measurements by Jeol machine (SEM5600LV). Coated Cu by Silver, Gold and Nickel are used as skimmers. Table 2 shows the variations of the concentration percentages of the coated Cu which are used as skimmers after working conditions in plasma. Figs. 2 and 3 show SEM micrographs of copper

Table 2
Different coated materials concentrations before and after working in the plasma of the ICP-MS for a period of 1 h (measured by EDS method)

Element	Material					
	Skimmer Au		Skimmer Ag		Skimmer Ni	
	Before	After	Before	After	Before	After
Au%	83.61	0.09	–	–	–	–
Cu%	16.39	99.91	46.46	99.99	–	31.55
Ag%	–	–	53.54	0.1	–	–
Ni%	–	–	–	–	85	68.44
Cr%	–	–	–	–	15	0.01

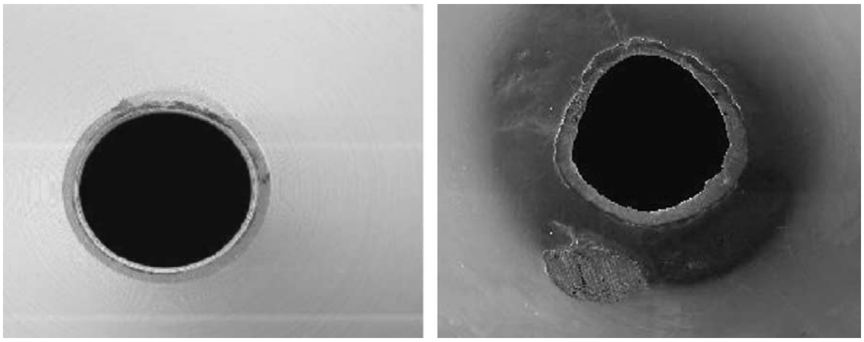

Fig. 2. SEM micrographs of copper skimmer cone coated by gold before working in the plasma (left) and after working in the plasma (right).

and aluminum skimmer cones, respectively, which are coated by gold before and after working in the plasma.

Inspection of Table 2 shows a real change in the material concentration of the skimmers. At the same time polyatomic from the skimmer material and Ar, O, H, N and C combinations appear in their different background spectra. Figs. 4 and 5 show a decrease of ion intensities of gold and gold polyatomic ions (AuAr, AuO, AuH, AuN and AuC) as a function of time, while an increase of copper and copper polyatomic ions (CuAr, CuO, CuH, CuN and CuC) as a function of time. Fig. 6 shows the relation between the normalized ion intensities (100%) of Au/Cu, Ni/Cu, Cr/Cu and Ag/Cu with time (min). Ni and Cr take more time to evaporate rather than Au and Ag.

Moreover, aluminum is used as a skimmer cone and copper is used as a sampler cone. Mass spectrometric measurements of Al and Cu ion intensities at the beginning of plasma operation shows that their Al/Cu intensity ratio is 13.97. EDS measurements of the skimmer elemental concentrations, as presented in Table 3, shows that this ratio reflects the amount of Cu in the used Al skimmer material. In the next step of this work, the Al skimmer is coated by Au and it is found that the ion intensity of Au decreases by time, meanwhile the ion intensity of Al increases by time as shown in Figs. 7 and 8. Table 4 shows the ion intensities of the background spectrum as formed from different combination.

Table 5 shows the heats of formation of the polyatomic species AuX, AgX, NiX, CrX and CuX, where X = Ar, O, N, C and H, as calculated by the Gaussian program G94W. In general, it is found that the heats of formation of polyatomic species YAr^+, YH^+ and YO^+, where Y = Au, Cu, Ag and Ni, are arranged

Fig. 3. SEM micrographs of aluminum skimmer cone coated by gold before working in the plasma (left) and after working in the plasma (right).

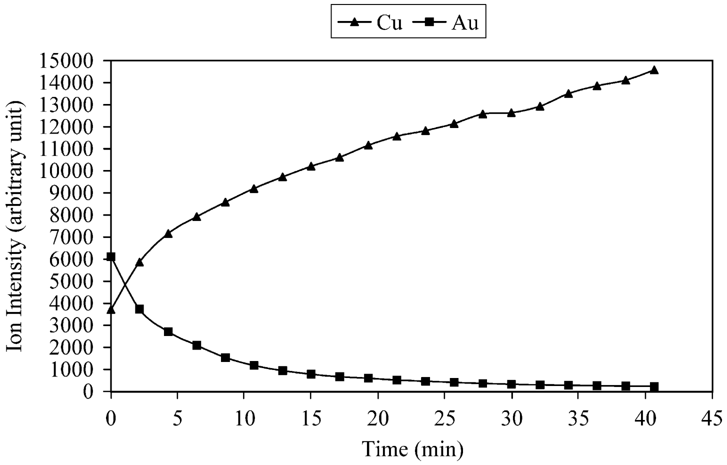

Fig. 4. Variation of Cu and Au ion intensities during the plasma working condition by time (the skimmer is Cu coated by Au).

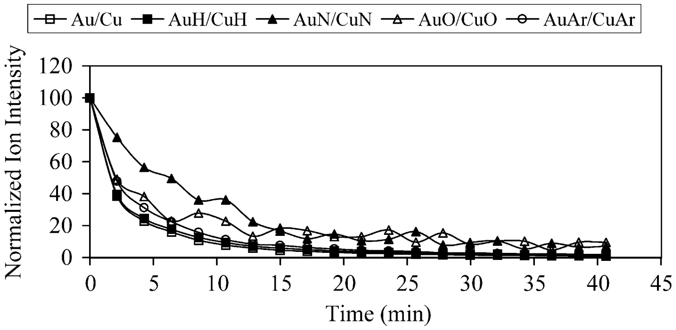

Fig. 5. Decrease of Au/Cu, AuH/CuH, Au/N/CuN, AuO/CuO and AuAr/CuAr ion intensities ratios induced from coated Cu skimmer by Au as a function of time.

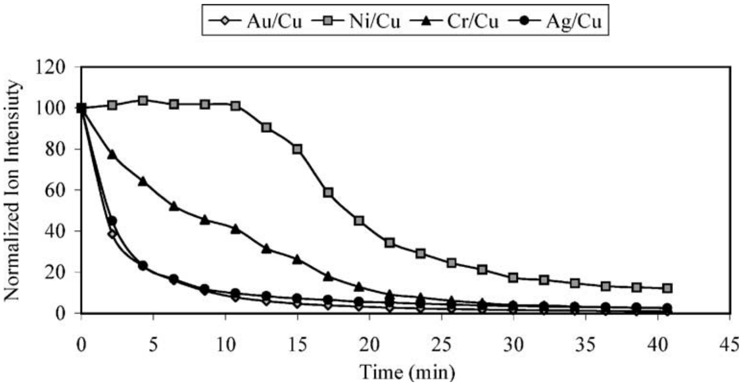

Fig. 6. Normalized ion intensities of skimmer materials (Au, Ag, Ni and Cr) relative to Cu as a function of time.

Table 3
Concentration percentages of major elements in Al and Cu skimmer cones as measured using energy dispersive spectrometer (EDS)

Element	Al skimmer	Cu skimmer
O	2.10 ± 0.13	0.71 ± 0.07
Al	70.50 ± 0.24	0.06 ± 0.02
Si	7.09 ± 0.09	–
Mn	0.18 ± 0.05	–
Fe	2.24 ± 0.07	0.06 ± 0.03
Ni	0.70 ± 0.07	–
Cu	5.31 ± 0.14	97.39 ± 0.3
Zn	11.88 ± 0.2	0.13 ± 0.01

in the manner as $\Delta H_f(\mathrm{YAr}^+) < \Delta H_f(\mathrm{YH}^+) < \Delta H_f(\mathrm{YO}^+)$.

Formation of polyatomic ions from the material of the skimmer cone and the background species is explained as follows: ions and electrons flow through the sampler orifice into the vacuum system, where a supersonic jet is formed. The central section of the jet flows through the skimmer orifice. Shock waves caused by collisions between fast atoms from the jet and the tip of the skimmer cone induce ejection of atoms of the skimmer material. Recombination between the ejected atoms and background gas atoms are possible in the region between skimmer and pullout cone.

It had been proposed that the gas flow through the orifice led to an increase in the electron density at the orifice and this is responsible for the secondary

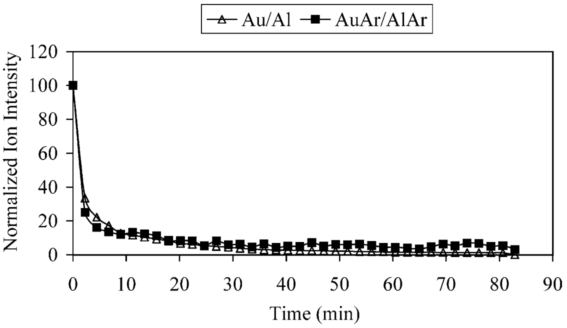

Fig. 8. Variation of Au/Al and AuAr/AlAr ratios induced from coated Al skimmer by Au as a function of time.

Table 4
Intensities of polyatomic ions (in the background spectra) relative to the ion intensities of skimmer materials X (X = Au, Cu, Ag, Ni and Al) in the ICP ion source

Species	Species intensity relative to X (X = Au, Cu, Ag, Ni and Al)	Species	Species intensity relative to X (X = Au, Cu, Ag, Ni and Al)
AuAr^+	3.1×10^{-3}	AuH^+	12.5×10^{-3}
CuAr^+	5.1×10^{-3}	CuH^+	1.3×10^{-3}
AgAr^+	4.2×10^{-3}	AgH^+	2.4×10^{-3}
NiAr^+	3.5×10^{-3}	NiH^+	3.6×10^{-3}
AlAr^+	75.3×10^{-3}	AlH^+	88.4×10^{-3}
AuO^+	0.1×10^{-3}	AuN^+	0.9×10^{-3}
CuO^+	4.5×10^{-3}	CuN^+	0.008×10^{-3}
AgO^+	6.8×10^{-3}	AgN^+	0.06×10^{-3}
NiO^+	44.0×10^{-3}	NiN^+	0.07×10^{-3}
AlO^+	5.1×10^{-3}	AlN^+	97.3×10^{-3}

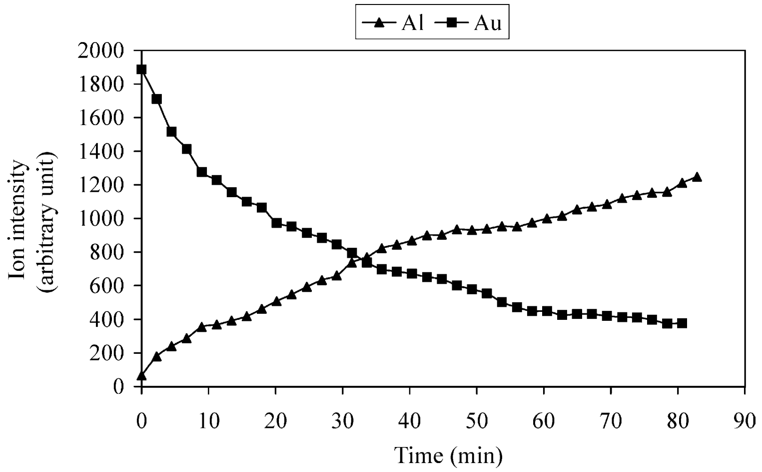

Fig. 7. Variation of Al and Au ion intensities induced from coated Al skimmer by Au as a function of time.

Table 5
Heats of formation of argides, oxides, hydrides and nitrides polyatomic ions which are formed from Au, Cu, Ag and Ni–Cr skimmer materials

Species	ΔH_f (kJ/mol)		Species	ΔH_f (kJ/mol)	
	This work	Reference [19]		This work	Reference [19]
$AuAr^+$	1251	–	AuH^+	1369	–
$CuAr^+$	942	–	CuH^+	1222	–
$AgAr^+$	877	–	AgH^+	1161	1170
$NiAr^+$	186	–	NiH^+	701	–
$CrAr^+$	948	–	CrH^+	1331	–
$AlAr^+$	951	–	AlH^+	1172	–
AuO^+	1407	–	AuN^+	1709	–
CuO^+	1364	–	CuN^+	1569	–
AgO^+	1386	–	AgN^+	1524	–
NiO^+	1022, 1340[a]	1234	NiN^+	1243	–
CrO^+	861, 1178[a]	1000	CrN^+	1386	–
AlO^+	1517	–	AlN^+	1461	–

[a] Using the value $\Delta H_f(O) = 437.9$ kJ/mol.

discharge [8,10,18,20,21]. Since the sampler and the skimmer of the JMS-PLASMAX2 mass spectrometer are maintained at high voltage (6 kV), it is expected that a high electron density could be accumulated on the sampler and the skimmer. However, Houk et al. [18,22–24] reported that no discharge was observed by using a flat top sampler (orifice diameter: 0.5 mm) under the same operating conditions which gave a visible arc with a sharp edged conical sampler of the same orifice diameter. In the current experiment, a flat top sampler cone and sharp edged conical skimmer (height = 7.56 mm and diameter = 0.9 mm) are used. Therefore, it is expected that secondary discharges, which may erode the orifice, can occur at the skimmer cone. This evidence is observed by Sakata and Kawabata [25], where they verify the presence of an orange–white discharge around the skimmer cone. On the other side, many authors [1,8,10,18,20] reported

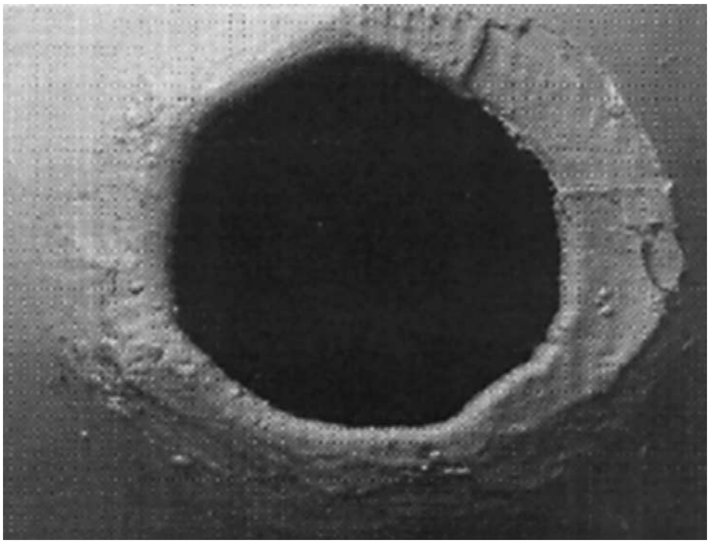

Fig. 9. SEM-image of copper skimmer cone covered by aluminum when aqueous solution of aluminum introduced to ICP-MS.

that the secondary discharge could appear around the sampler orifice.

On the other side, if aluminum sample digested and introduced to the ICP-MS, the orifice of the skimmer cone is completely covered by aluminum while a little accumulation is observed about the sampler orifice. Fig. 9 shows SEM-EDS image of the skimmer cone covered by aluminum oxide (98%). The previous remarks showed that skimmer is largely participated in the formation of polyatomic due to their interaction in the shock waves.

References

[1] R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray, C.E. Taylor, Anal. Chem. 52 (1980) 2283.
[2] M.A. Vaughan, G. Horlick, Appl. Spectrosc. 40 (1986) 434.
[3] N.M. Reed, R.O. Cairns, R.C. Hutton, Y. Takaku, J. Anal. Atom. Spectrum. 9 (1994) 881.
[4] E.H. Evans, J.J. Giglio, J. Anal. Atom. Spectrum. 8 (1993) 1.
[5] H. Niu, R.S. Houk, Spectrochim. Acta, Part B 8 (1996) 779.
[6] E.H. Evans, L.J. Ebdon, J. Anal. Atom. Spectrum. 5 (1990) 425.
[7] D.J. Douglas, J.B. French, Spectrochim. Acta 41B (1986) 197.
[8] R.S. Houk, V.A. Fassel, H.J. Svec, Dynamic Mass Spectrom. 6 (1981) 234.
[9] A.R. Date, A.L. Gray, Analyst 106 (1981) 1255.
[10] A.L. Gray, A.R. Date, Dynamic Mass Spectrom. 6 (1981) 252.
[11] D.J. Douglas, J.B. French, J. Anal. Atom. Spectrom. 3 (1988) 743.
[12] D.J. Douglas, L.A. Kerr, J. Anal. Atom. Spectrom. 3 (1988) 749.
[13] E.H. Evans, J.A. Caruso, Spectrochim. Acta 47B (1992) 1012.
[14] K.E. Jarvis, P. Mason, T. Platzner, J.G. Williams, J. Anal. Atom. Spectrom. 13 (1998) 689.
[15] D. Günther, H.P. Longerich, S.E. Jackson, Forsythe, Freseius J. Anal. Chem. 355 (1996) 771.
[16] A.R. Date, A.L. Gray, Spectrochim. Acta 38B (1983) 27.
[17] A.L. Gray, A.R. Date, Analyst 108 (1983) 1033.
[18] D.J. Douglas, J.B. French, Spectrochim. Acta 41B (1986) 197.
[19] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard, J. Phys. Chem. Ref. Data 1 (1988).
[20] A.L. Gray, A.R. Date, Spectrochim. Acta 38B (1983) 27.
[21] T.N. Olney, Wei. Chem, D.J. Douglas, J. Anal. Atom. Sepectrom. 14 (1999) 9.
[22] R.S. Houk, V.A. Fassel, G.D. Flesch, H.J. Svec, A.L. Gray, C.E. Taylor, Anal. Chem. 52 (1981) 2283.
[23] H.S. Niu, K. Hu, R.S. Houk, Sepctrochim. Acta 46B (1991) 508.
[24] H. Niu, R.S. Houk, Spectrochim. Acta 51B (1996) 779.
[25] K. Sakata, K. Kawabata, Spectrochim. Acta 49B (1994) 1027.